

Moumita Maiti* and Susanta Lahiri

Measurement of yield of residues produced in $^{12}\text{C} + ^{\text{nat}}\text{Y}$ reaction and subsequent separation of ^{97}Ru from Y target using cation exchange resin

Abstract: This paper reports the yield of no-carrier-added (NCA) radionuclides produced in $^{12}\text{C}^{6+}$ induced reaction on natural yttrium target at 10 different incident energies in the range of 40 to 75 MeV by the stacked-foil technique, followed by off-line γ -ray spectroscopy. It also reports the radiochemical separation of NCA ^{97}Ru from the bulk yttrium target. ^{97}Ru was produced in the yttrium matrix through $^{89}\text{Y}(^{12}\text{C}, 4n)^{97,97m}\text{Rh}(\text{EC})^{97}\text{Ru}$ and $^{89}\text{Y}(^{12}\text{C}, p3n)^{97}\text{Ru}$ reactions along with the radioisotopes ^{98}Rh , ^{97}Rh , ^{97m}Rh , ^{93}Tc , ^{94}Tc , ^{95}Tc and ^{93m}Mo . Irradiated target was allowed to cool for the complete decay of short-lived residues and ^{97}Ru was then separated from the bulk yttrium using the cation exchanger DOWEX-50WX4 in an ion exchange column as well as *via* solid-liquid extraction (SLX). A total of ~88% NCA ^{97}Ru was separated in column chromatography without any contamination of bulk, whereas quantitative separation of NCA Ru was achieved in SLX.

Keywords: ^{12}C -induced reaction, Yttrium, NCA ^{97}Ru , Batch yield, Stacked-foil technique, Radiochemical separation, DOWEX-50WX4.

DOI 10.1515/ract-2014-2277

Received April 19, 2014; accepted July 15, 2014

1 Introduction

Ruthenium has a number of oxidation states (oxidation number ranging from 0 to +8 and -2); hence it forms a wide range of complexes, which are eventually finding a variety of applications. The rich chemical property of ruthenium has been exploited in medical science. Previously ^{103}Ru (39.25 d) was used in labelling ligands as it is obtained easily by neutron activation of naturally

abundant ^{102}Ru . However, ^{97}Ru [$T_{1/2} = 2.83$ d, EC decay 100%, only two intense γ -rays: 215.70 keV (85.62%) and 324.49 keV (10.79%)] is a better choice for *in-vivo* applications, if it is obtained in a no-carrier-added (NCA) state. ^{97}Ru may serve as a very suitable radionuclide among other Ru radionuclides for delayed studies of diagnosis as well as therapy by attaching it to a suitable carrier or ligand [1, 2]. It is even possible to use ^{97}Ru as a tracer to measure the backside wear rate on tibial inserts [3, 4].

The NCA ^{97}Ru has mostly been produced through light ion (p , ^3He and α -particle) induced reactions on suitable targets such as metallic technetium (^{99}Tc), rhodium, silver, molybdenum, etc. [5–12]. Though it is seen from the literature that proton induced reactions ($p + ^{99}\text{Tc}$, $p + ^{\text{nat}}\text{Rh}$, $p + ^{\text{nat}}\text{Ag}$) offer high yield of ^{97}Ru , but they are associated with several disadvantages such as use of radioactive target (^{99}Tc), non-availability of required projectile energy (~200 MeV) in common accelerators, etc. In case of ^3He - or α -particle induced reaction on natural molybdenum, ^{97}Ru is produced along with ^{95}Ru , ^{103}Ru and technetium radionuclides such as ^{93}Tc , ^{94}Tc , ^{95}Tc , ^{96}Tc . We also proposed a new route to produce ^{97}Ru in ^7Li -induced reaction on natural niobium target [13]. It is interesting to note that all the established methods for production of ^{97}Ru also produce radionuclidic impurities which have longer half-lives than ^{97}Ru . For example, proton induced reaction coproduces ^{95m}Tc (61 d), ^{96}Tc (4.28 d), etc. The α -particle induced reactions, and even the ^7Li induced reaction co-produce ^{96}Tc . Recently we reported the production of NCA ^{97}Ru *via* ^{12}C -induced reaction on natural yttrium target [14]. The novelty of this production route is that there is no co-produced radionuclide which has longer half-life than ^{97}Ru . We also reported the batch yield of various radionuclides produced *via* $^{12}\text{C} + ^{89}\text{Y}$ reactions at a particular energy, i.e., at 75 MeV projectile energy [14]. As a part of our continuous effort, this article illustrates estimation of batch yield of the evaporation residues produced in the $^{12}\text{C} + ^{89}\text{Y}$ reaction by the stacked-foil technique at 10 different incident energies, covering a wide range of projectile energy.

In order to separate NCA Ru from the target matrix, various chemical separation methodologies, namely dis-

*Corresponding author: Moumita Maiti, Department of Physics, Indian Institute of Technology Roorkee, Roorkee-247667, Uttarakhand, India, e-mail: moumifph@iitr.ac.in

Susanta Lahiri: Chemical Sciences Division, Saha Institute of Nuclear Physics, 1/AF Bidhannagar, Kolkata-700064, India

tillation, solvent extraction, ion-exchange method, precipitation, liquid-liquid extraction (LLX), solid liquid extraction (SLX), etc., have been developed so far [1, 5, 6, 8–16]. In the past, distillation technique was largely used to separate NCA ^{97}Ru from the ^{99}Tc (2.111×10^5 a) and ^{103}Rh (100% abundant) targets. Usually NCA Ru is oxidized using KMnO_4 , HClO_4 , CrO_3 , etc., and distilled from the concentrated acid medium. However, this method is not suitable if Tc is present in the active mixture either as target material or as a coproduced radionuclide. This is because technetium forms technetium oxides like TcO_4^- , Tc_2O_7 and is thereby distilled along with the desired NCA $^{97}\text{RuO}_4$. It is therefore difficult to avoid contamination and in most cases authors remained silent about it.

Comar and Crouzel [9] separated NCA ^{97}Ru by solvent extraction technique using CCl_4 from ^{95}Tc and bulk Mo. Purity of ^{97}Ru achieved was more than 99.9%. The NCA ^{97}Ru was precipitated by Fe(OH)_3 from the mixture of NCA Ru, NCA Tc and bulk Mo [10]. ^{97}Ru was also separated from bulk Mo and coproduced Tc by ion-exchange technique using SnO_2 column, followed by purification of ^{97}Ru in an anion-exchange column Bio-Rad AG1-X8 in nitrate form [12]. Lahiri *et al.* [15, 16] reported LLX and separation of NCA Ru radionuclide using liquid anion exchanger trioctylamine (TOA) or liquid cation exchanger di-(2-ethylhexyl)phosphoric acid (HDEHP) dissolved in cyclohexane as organic phase and HCl as aqueous phase. We followed the similar footsteps while separating ^{97}Ru from bulk Nb and coproduced NCA Tc using HDEHP in LLX and cation exchange resin DOWEX-50WX4 in SLX from HCl medium [13]. The production of ^{97}Ru by different nuclear reactions and the corresponding radiochemical separation procedure reported so far is listed in Table 1.

Our recent paper [14] described the method of separation of ^{97}Ru from bulk target matrix and co-produced radionuclides by liquid ion exchangers like trioctylamine (TOA) and di-(2-ethylhexyl) phosphoric acid (HDEHP). The present paper extends the radiochemical separation studies of NCA ^{97}Ru from the bulk yttrium target by chromatography and SLX.

2 Experimental

It has been learned from our earlier study that ^{97}Ru will be produced in $^{12}\text{C} + ^{89}\text{Y}$ reaction along with other radionuclides, like ^{94}Tc , ^{95}Tc , ^{98}Rh , ^{99}Rh below 70 MeV projectile energy. Further increase in projectile energy will introduce the production of several other short-lived radionuclides namely ^{93}Tc , ^{93m}Mo , ^{96}Rh and long-lived ^{96}Tc [14]. There-

Table 1: Production of ^{97}Ru in various reactions, separation and the associated impurities.

Sl. No	Production route, Projectile energy	Method of separation used; remarks	Ref.
1.	$^{103}\text{Rh}(p, 2p5n)^{97}\text{Ru}$, 200 MeV	Distillation of Ru from H_2SO_4 medium in presence of permanganate; impurity not mentioned	[1]
2.	$^{103}\text{Rh}(p, 2p5n)^{97}\text{Ru}$, 67.5 MeV	^{97}Ru was separated by distillation from Rh and Pd; however, ^{97}Ru fraction contains Tc impurity	[5, 6]
3.	$^{99}\text{Tc}(p, 3n)^{97}\text{Ru}$, 50 MeV	^{97}Ru was separated by distillation from bulk ^{99}Tc and other Tc impurities	[7, 8]
4.	(i) $^{nat}\text{Mo}(\alpha, xn)^{97}\text{Ru}$, 15.8, 18 and 22 MeV (ii) $^{nat}\text{Mo}({}^3\text{He}, xn)^{97}\text{Ru}$, 18.3, 26.7 and 30 MeV	^{97}Ru was separated from bulk Mo by solvent extraction. No fate of Tc impurities is given.	[9]
5.	$^{nat}\text{Mo}(\alpha, xn)^{97}\text{Ru}$, 22–30 MeV	followed Ref. [9]	[10]
6.	(i) $^{nat}\text{Mo}(\alpha, xn)^{97}\text{Ru}$, up to 28 MeV (ii) $^{nat}\text{Mo}({}^3\text{He}, xn)^{97}\text{Ru}$, up to 36 MeV	^{97}Ru was separated by solvent extraction [9] and distillation method	[11]
7.	$^{nat}\text{Mo}(\alpha, xn)^{97}\text{Ru}$, 30 MeV	^{97}Ru was separated from Mo and Tc by ion exchange column	[12]
8.	$^{93}\text{Nb}({}^7\text{Li}, 3n)^{97}\text{Ru}$, 32 MeV	^{97}Ru was separated from Nb and Tc by liquid-liquid extraction	[13]
9.	$^{89}\text{Y}({}^{12}\text{C}, 4n)^{97}\text{Rh(EC)}$ $^{97}\text{Ru} + {}^{89}\text{Y}({}^{12}\text{C}, 4n)^{97m}\text{Rh}$ (EC/IT) ^{97}Ru , 75 MeV	^{97}Ru was separated from Y and Tc by liquid-liquid extraction	[14]

fore a projectile energy window of 65–70 MeV was chosen for the optimum production of ^{97}Ru .

Natural yttrium (^{89}Y) foil (99.9% purity) procured from Alfa Aesar was rolled properly to produce uniform thin self-supporting foils of 2 mg/cm^2 thickness. The yttrium foils and the aluminium catcher foils of 1.5 mg/cm^2 thickness procured from MERCK were mounted on aluminium rings of 0.5 mm thickness (12 mm inner and 22 mm outer diameter). Each yttrium foil accompanies an aluminium catcher and 3 such yttrium-aluminium (target-catcher) combinations made a target stack. The target stack thus prepared was bombarded by ${}^{12}\text{C}^{6+}$ ions with an

average beam current of ~90 nA. A total of 4 such target stacks were irradiated separately varying the projectile energy with an overlap between them. In each irradiation, integrated charge was measured by an electron suppressed Faraday cup placed at the back of the target assembly. On average ~1000 μC charge was collected in each irradiation. The recoiled residual products, if any, in the beam direction were stopped completely in the large area of the catcher foils. The irradiation experiments were carried out at the BARC-TIFR Pelletron, Mumbai, India. Energy loss in each yttrium and aluminium foils was estimated by Stopping and Range of Ions in Matter (SRIM) [17]. The projectile energy at the target is the average of incident and outgoing energy.

At the end of bombardment (EOB), each irradiated foil was assayed to estimate the activity of the residues by off-line γ -ray spectrometry using an HPGe detector having resolution of 2.13 keV at 1332 keV coupled to a PC-based MCA in a regular time interval for sufficient long period. The detector was calibrated using known standard sources: ^{152}Eu (13.537 a), ^{133}Ba (10.54 a) and ^{137}Cs (30.0 a). The background subtracted peak area count of characteristic γ -ray energy is the measure of yield of the corresponding radionuclide.

An extra yttrium foil of 4 mg/cm^2 was irradiated separately with 70 MeV $^{12}\text{C}^{6+}$ ions for 3 h with an average beam current of ~90 nA to develop radiochemical separation of NCA ^{97}Ru from the yttrium target matrix. The yttrium isotope required to monitor the destination of the bulk yttrium during radiochemical separation is hardly produced in $^{12}\text{C} + ^{89}\text{Y}$ interaction. Therefore another yttrium foil of 3 mg/cm^2 was irradiated by 22 MeV protons for 2 h at ~600 nA beam current to produce ^{88}Y (106.6 d) in the yttrium matrix required for the radiochemical separation study.

2.1 Radiochemical separation

The ^{12}C and proton irradiated yttrium foils were cooled for 5 days and then 3.5 mg of ^{89}Y foils were separately dissolved in minimum volume of 0.1 M HCl. The NCA $^{88,89}\text{Zr}$ isotopes produced in proton irradiation were separated from the bulk yttrium using our previous report [18] and the yttrium solution containing ^{88}Y was kept in 0.1 M HCl. The ^{88}Y tracer thus prepared was spiked with the ^{12}C irradiated yttrium solution and evaporated to dryness to arrive at the same chemical form for both ^{88}Y tracer and bulk yttrium. The residue was then dissolved in 0.01 M HCl to prepare stock solution that contains ruthenium (^{97}Ru) and yttrium uniformly. The active stock solution was used

to explore the radiochemical separation of ^{97}Ru by ion-exchange method.

Before chromatographic separation, SLX in batch mode was performed using cation exchange resin DOWEX-50WX4 procured from Sigma Aldrich, varying the concentration of HCl. Before extraction, 1 g resin was conditioned for 30 min with 3.5 mL HCl of each concentration. For SLX, 200 μL of active stock solution was added to the aqueous HCl and was shaken vigorously for 10 min with the help of a mechanical shaker. Supernatant was separated by centrifugation (~5000 rpm) and the distribution of NCA Ru and bulk yttrium between the supernatant and resin were measured by γ -ray spectrometry.

A glass column of 165 mm length and 5.5 mm internal diameter was tightly packed with 3.5 g of DOWEX-50WX4 resin. The resin was preconditioned with dilute HCl for 5 h. The active solution (5 mL) containing NCA ^{97}Ru and bulk yttrium was loaded on to the column and then radioisotopes were eluted with 0.1 M HCl initially and later with 6 M HCl, controlling a flow rate of ~2 drops/min. Elutes from the column were collected in eppendorfs in 10 min intervals and were assayed sequentially by γ -ray spectrometry maintaining the same geometry. The photo peaks of 215.7 and 898.1 keV were monitored to analyze the fate of ^{97}Ru and yttrium (^{88}Y) respectively. All chemicals or reagents used in this experiment were of analytical grade and were used without further purification.

3 Results and discussion

Analysis of off-line γ -ray spectra depicts the production of ^{98}Rh (8.7 min), ^{97}Rh (30.7 min), ^{97m}Rh (46.2 min), ^{97}Ru (2.83 d), ^{93}Tc (2.75 h), ^{94}Tc (4.9 h), ^{95}Tc (20.0 h) and ^{93m}Mo (6.85 h) in various yttrium foils irradiated at different projectile energies. Nuclear spectroscopic data of the products are tabulated in Table 2 [19]. A representative γ -ray spectrum of the ^{12}C (70 MeV) irradiated natural yttrium foil (4 mg/cm^2) collected after 1 h of EOB is presented in Figure 1. Thick target yield of the residual radionuclides at 10 different incident energies (42.4, 49.2, 51, 55.5, 57.2, 61.3, 63, 66.7, 68.6, and 73.8 MeV) have been measured at EOB covering the 40–75 MeV energy range. All possible errors related to the yield measurement have been considered and the data have been presented up to 95% confidence level. Batch yield of short-lived ($T_{1/2} < 5$ h) radionuclides, ^{98}Rh , ^{97}Rh , ^{97m}Rh , ^{93}Tc , ^{94}Tc and comparatively long-lived ($T_{1/2} > 5$ h) radionuclides, ^{93m}Mo , ^{95}Tc and ^{97}Ru are tabulated in Table 3. In order to understand the yield profile of the various products, theoretical excitation functions obtained from

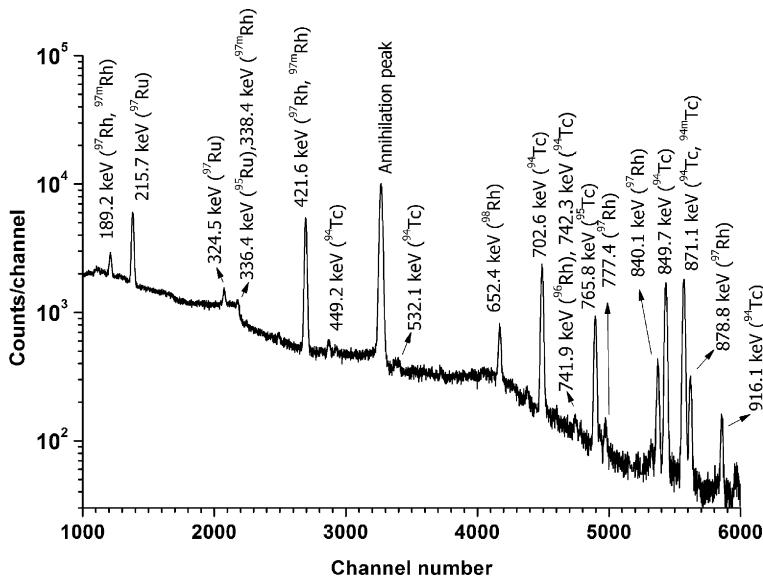


Fig. 1: The γ -ray spectrum of the ^{12}C (70 MeV) irradiated natural yttrium foil after 1 h of EOB.

Table 2: Nuclear spectroscopic data of various radionuclides produced in $^{89}\text{Y} + ^{12}\text{C}$ reaction [19].

Radionuclide	$T_{1/2}$	γ -rays in keV (Intensity)
^{97}Ru	2.83 d	215.70 (85.62%), 324.49 (10.79%)
^{98}Rh	8.72 min	652.6 (97%)
^{97}Rh	30.7 min	421.55 (74.63%), 840.13 (12%)
^{97m}Rh	46.2 min	189.21 (48.5%)
^{93}Tc	2.75 h	1362.94 (66.2%), 1520.28 (24.4%)
^{94}Tc	4.9 h	702.67 (99.6%), 849.74 (95.7%), 871.05 (99.9%)
^{95}Tc	20.0 h	765.789 (93.8%)
^{93m}Mo	6.85 h	263.049 (57.4%), 684.693 (99.9%), 1477.138 (99.1%)

PACE4 [20] for $^{12}\text{C} + ^{89}\text{Y}$ reaction are shown in Figure 2. It is observed that the trends of measured yields of ^{98}Rh , ^{97}Rh , ^{94}Tc and ^{93}Tc agree with those of the corresponding excitation functions (Figure 2) showing maxima around the theoretical prediction. Measured yields of ^{97}Ru and ^{93m}Mo were also found to follow the same trend with the theory. However, the maximum yield of ^{95}Tc was measured at 61 MeV while it was expected around 55 MeV. As a result, production of ^{95}Tc cannot be avoided by choosing the particular projectile energy window. Production of NCA ^{97}Ru is contributed from (i) direct production through $^{nat}\text{Y}(^{12}\text{C}, p3n)^{97}\text{Ru}$ reaction, and (ii) indirect production

via $^{nat}\text{Y}(^{12}\text{C}, 4n)^{97}\text{Rh}$ (EC) ^{97}Ru and $^{nat}\text{Y}(^{12}\text{C}, 4n)^{97m}\text{Rh}$ (EC: 94.4%, IT: 5.6%) ^{97}Ru reactions. Because of short half-lives all other residues decay mostly to a stable isotope within a day and ^{97}Ru (2.83 d) will be abundant along with ^{95}Tc (20. h). Although a signature of the production of ^{96}Tc was observed in the yttrium foils irradiated by ^{12}C ions above 70 MeV, its yield could not be measured due to low activity.

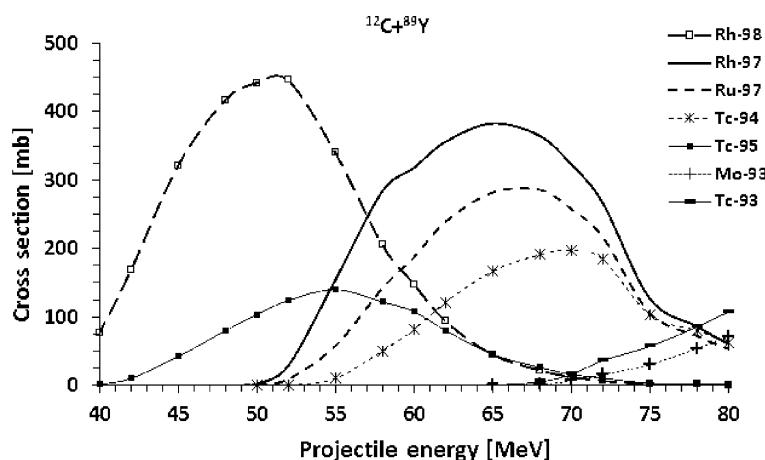
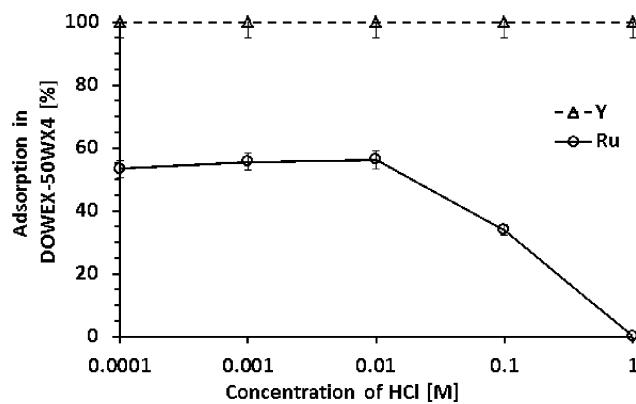
It should be mentioned that in case of the separate yttrium foil irradiated by 70 MeV ^{12}C projectiles to explore the radiochemical separation of ^{97}Ru , the exit energy of the projectile was calculated as 65 MeV using SRIM [17]. As the radiochemical separation was performed after 5 days cooling of the target after EOB, most of the ^{95}Tc activity had decayed by the time; hence during radiochemical separation ^{95}Tc present in each fraction was below the detection limit.

3.1 Solid liquid extraction (SLX)

The extraction profile of NCA Ru and bulk Y obtained in SLX, where solid cation-exchange resin DOWEX-50WX4 was used with varying concentration of HCl (1×10^{-4} –1 M), is shown in Figure 3. Change of HCl concentration had hardly any effect on the quantitative adsorption of bulk Y in the solid resin. This is because yttrium remains as Y^{3+} throughout the acid range and hence it is adsorbed by the DOWEX-50WX4. This observation is in agreement with our earlier observations [14, 18, 21]. It is also observed that ~50% NCA Ru was adsorbed to the resin at pH 4–2, but

Table 3: Batch yield of residues at EOB.

Energy (MeV)	Yield of radionuclides in [kBq/ μA h]							
	^{97}Ru	^{98}Rh	^{97}Rh	^{97m}Rh	^{93}Tc	^{94}Tc	^{95}Tc	^{93m}Mo
42.4	0.7±0.1	399±38	—	—	—	—	7±1.5	—
49.2	1.9±0.2	1010±91	14±1	4±0.5	—	—	39±3	—
51	7.6±0.8	1316±131	76±8	15.3±1.5	—	—	51±5	—
55.5	36±4	945±75	355±32	41±5	—	24±2	76±8	—
57.2	47±5	827±66	432±39	53±5	—	44±4	71±7	—
61.3	95±9	550±33	842±59	71±7	—	142±17	86±9	0.6±0.1
63	109±12	516±67	852±60	76±8	—	184±20	86±10	—
66.7	110±11	215±17	796±64	62±7	—	260±26	64±6	6±0.7
68.6	108±12	208±19	699±70	50±6	25±4	275±36	59±9	8±1.6
73.8	93±11	70±9	542±49	32±3	89±9	371±37	44±5	30±3

**Fig. 2:** Theoretical excitation functions of the radionuclides produced in $^{12}\text{C} + ^{89}\text{Y}$ reaction.**Fig. 3:** Adsorption of NCA Ru and bulk Y in DOWEX-50WX4 (1 g) as a function of HCl concentration.

increase in acidity reduced the adsorption of NCA Ru, and at 1 M HCl quantitative separation was achieved. A high separation factor of 6.7×10^5 (D_Y/D_{Ru}) was achieved at the optimum condition. Distribution coefficients and sep-

Table 4: Distribution coefficients (D) and separation factor (SF) of NCA Ru and bulk Y in SLX at optimal condition and number of theoretical plates (N) for each peak shown in Figure 4.

SLX	Chromatography				
	Experimental condition: HCl (1 M)/DOWEX-50WX4 (1 g)		Values of N by half height method		
D_Y	D_{Ru}	$SF (D_Y/D_{\text{Ru}})$	Ru	Y	
511	7.6×10^{-4}	6.7×10^5	Peak 'a' 17	Peak 'b' 178	246

aration factors obtained at the optimal experimental condition are presented in Table 4.

3.2 Chromatographic separation

Figure 4 shows the elution profile of ^{97}Ru and bulk Y. It is observed that ~68% pure ^{97}Ru was eluted by 0.1 M HCl in first 3 h. Yttrium was retained on the column quantita-

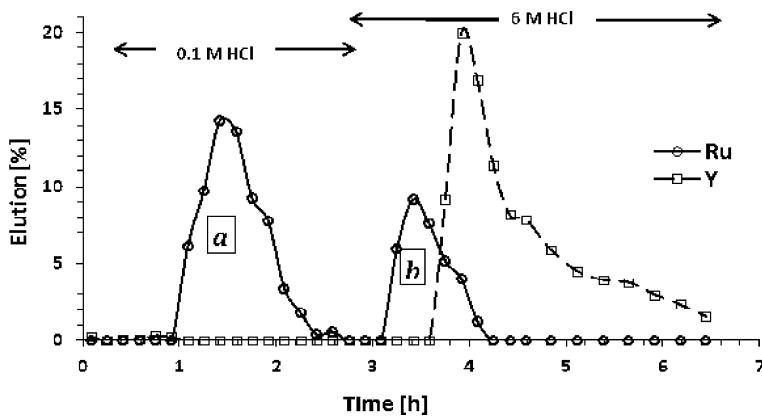


Fig. 4: Chromatogram shows the elution of NCA Ru and bulk Y. The peaks labelled as *a* and *b* both are for Ru.

tively along with the rest of ^{97}Ru (33%). Use of 6 M HCl eluted first the remaining ^{97}Ru and then bulk yttrium. On elution with 6 M HCl, about 20% pure ^{97}Ru was eluted first and the rest was eluted with bulk yttrium. Thus a total of 88% separation of ^{97}Ru was achieved from the bulk matrix. Two separate and distinct peaks in the elution curve of Ru are possibly due to the formation of different species of Ru. Ru contains Ru(III) and Ru(IV) species in HCl solution. The Ru(IV)-chloro complexes: $[(\text{RuOH})_2(\text{OH})_2\text{Cl}_6]^{2-}$, $[(\text{RuOH})_2\text{Cl}_8]^{2-}$, $[\text{Ru}(\text{H}_2\text{O})\text{Cl}_5]^-$, $[\text{Ru}(\text{OH})_2\text{Cl}_4]^{2-}$, etc. in aqueous HCl not only undergo aquation, hydrolysis but are also reduced to Ru(III) complexes [22]. However, at room temperature these complexes are rather stable, but increase in temperature to 60–80 °C accelerates the reduction process. As a result, being mostly stable anions at room temperature (~22 °C), Ru(IV) species are not attracted by the resin, and are eluted from the column by 0.1 M HCl. Rest of Ru most likely forms Ru(III) species, such as $[\text{Ru}(\text{H}_2\text{O})_4\text{Cl}_2]^+$, $[\text{Ru}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$, etc., which were retained into the resin column. These Ru(III) species were eluted along with Y(III) by 6 M HCl [22, 23]. High separation factors of 2.8 [$\alpha = T_R(\text{Y})/T_R(\text{Ru}^a)$] and 1.2 [$\alpha = T_R(\text{Y})/T_R(\text{Ru}^b)$] were achieved, where ‘*a*’ and ‘*b*’ are the two peaks of Ru as shown in Figure 4. The number of theoretical plates was calculated and is tabulated in Table 4 for three separate peaks (two for Ru labelled as ‘*a*’ and ‘*b*’, and one for Y) using the half height method as given below:

$$N = 5.54 \left(\frac{T_R}{w_{1/2}} \right)^2 \quad (1)$$

where N is the number of theoretical plates, T_R denotes retention time and $w_{1/2}$ is the width of the peak at half height ($h/2$), if the peak height is h .

4 Conclusion

This report provides experimental measurement of yields of the residues produced in ^{12}C induced reaction on natural yttrium target at ten different projectile energies covering the range 40–75 MeV. Though the reactions produced several residues, they are mostly short-lived and ^{97}Ru will be abundant after one day cooling time along with ^{95}Tc . It is evident from the measured yield that the production of comparatively long-lived contaminant, ^{95}Tc , cannot be avoided by choosing a particular projectile energy window. However, due to long cooling of the target (5 d), ^{95}Tc mostly decayed out and became in negligible quantity. As a consequence, it was not possible to monitor the fate ^{95}Tc during the exploration of radiochemical separation. However, if required, high purity Ru activity can be achieved by separating ^{95}Tc following our earlier reports [13, 14].

The quantity of ^{97}Ru produced in this method is quite low compared to the other production routes; therefore this route is not suitable for clinical applications. However, if the requirement is purity rather than quantity, then in this route one can have ^{97}Ru free from other radionuclidian impurities after a suitable cooling time. Also the amount of ^{97}Ru radionuclide would be sufficient for any *in situ* tracer study.

Ion-exchange techniques, SLX and chromatography, were developed to separate NCA Ru from the yttrium target. Quantitative separation of NCA Ru was achieved in SLX with a high separation factor. In chromatographic separation, two separate species of NCA Ru were observed in the elution curve of Ru. A total of 88% NCA ^{97}Ru was separated from yttrium without any contamination of bulk. A high separation factor was obtained in this case too. The developed methods are one step, eco-friendly separation techniques, complementary to each other. Chromatographic separation indicates the formation of differ-

ent Ru species, namely Ru(IV) and Ru(III) under the experimental condition.

Acknowledgement: We sincerely thank the staff of BARC-TIFR pelletron facility, and the target laboratory of TIFR, Mumbai, for their cooperation and help. Financial support from the SINP-DAE 12 five year plan project “Trace Ultra-trace Analysis and Isotope Production (TULIP)” is sincerely acknowledged.

References

1. Srivastava, S. C., Som, P., Meinken, G., Sewatkar, A., Ku, T. H.: Ruthenium-97 labeled compounds-A new class of radiopharmaceuticals. Brookhaven National Laboratory Report BNL 24614 (1978).
2. Shao, H. S., Meinken, G. E., Srivastava, S. C., Slosman, D., Sacker, D. F., Som, P., Brill, A. B.: *In vitro* and *in vivo* characterization of ruthenium bleomycin compared to cobalt- and copper-bleomycin. *J. Nucl. Med.* **27**, 1044 (1986).
3. Warner, J. A., Gladkis, L. G., Timmers, H.: A new radioisotope tracing method of UHMWPE wear particle dispersion using Ru-97. *J. Mech. Behav. Biomed. Mater.* **4**, 776 (2011).
4. Warner, J. A., Gladkis, L. G., Smith, P. N., Scarvell, J. M., Timmers, H.: Demonstration of a new technique using radioisotope tracers to measure the backside wear rate on Tibial inserts, *Tribol. Lett.* **46**, 139 (2012).
5. Lagunas-Solar, M. C., Avila, M. J., Nvarro, N. J., Johnson, P. C.: Cyclotron production of no-carrier-added ^{97}Ru by proton bombardment of ^{103}Rh targets. *Int. J. Appl. Radiat. Isot.* **34**, 915 (1983).
6. Lagunas-Solar, M. C., Avila, M. J., Johnson, P. C.: Targetry and radiochemical methods for the simultaneous cyclotron production of no-carrier-added radiopharmaceutical-quality ^{100}Pd , ^{97}Ru and $^{101\text{m}}\text{Rh}$. *Appl. Radiat. Isotopes* **38**, 151 (1987).
7. Zaitseva, N. G., Rurarz, E., Vobecky, M., Hwan, K. H., Nowak, K., Tethal, T., Khalkin, V. A., Popinenkova, L. M.: Excitation function and yield for ^{97}Ru production in $^{99}\text{Tc}(p, 3n)^{97}\text{Ru}$ reaction in 20–100 MeV proton energy range. *Radiochim. Acta* **56**, 59 (1992).
8. Zaitseva, N. G., Stegailov, V. I., Khalkin, V. A., Shakun, N. G., Shishlyannikov, P. T., Bukov, K. G.: Metal technetium target and target chemistry for the production of ^{97}Ru via the $^{99}\text{Tc}(p, 3n)^{97}\text{Ru}$ reaction. *Appl. Radiat. Isotopes* **47**, 145 (1996).
9. Comar, D., Crouzel, C.: Ruthenium-97 preparation with a compact cyclotron. *Radiochim. Radioanal. Lett.* **27**, 307 (1976).
10. Gessner, M., Music, S., Babarovic, B., Vlatkovic, M.: Investigation of the preparation of ^{97}Ru . *Int. J. Appl. Radiat. Isotopes* **30**, 578 (1979).
11. Comparetto, G., Qaim, S. M.: A comparative study of production of short-lived neutron deficient isotopes $^{94,95,97}\text{Ru}$ in α - and ^3He -particle induced nuclear reactions on natural molybdenum. *Radiochim. Acta* **27**, 177 (1980).
12. Pao, P. J., Zhou, J. L., Silvester, D. J., Waters, S. L.: A rapid and simple separation of ^{97}Ru from irradiated molybdenum. *Radiochim. Radioanal. Lett.* **46**, 21 (1981).
13. Maiti, M., Lahiri, S.: Production and separation of ^{97}Ru from ^7Li activated natural niobium. *Radiochim. Acta* **99**, 359 (2011).
14. Maiti, M.: Production and separation of ^{97}Ru and coproduced ^{95}Tc from ^{12}C -induced reaction on natural yttrium target. *Radiochim. Acta* **101**, 437 (2013).
15. Lahiri, S., Mukhopadhyay, B., Das, N. R.: LLX separation of carrier-free $^{94,95,97,103}\text{Ru}$, $^{93,94,95,96,99\text{m}}\text{Tc}$ and $^{95,96}\text{Nb}$ produced in alpha-particle activated molybdenum by TOA. *J. Radioanal. Nucl. Chem.* **221**, 167 (1997).
16. Lahiri, S., Mukhopadhyay, B.: Liquid-Liquid extraction of Carrier-free radioisotopes produced in α -particle activated molybdenum target by HDEHP and TBP. *Appl. Radiat. Isotopes* **48**, 925 (1997).
17. Ziegler, J. F., Ziegler, M. D., Biersack, J. P.: SRIM-The stopping and range of ions in matter (2010). *Nucl. Instrum. Methods Phys. Res. B* **268**, 1818 (2010).
18. Dutta, B., Maiti, M., Lahiri, S.: Production of $^{88,89}\text{Zr}$ by proton induced activation of $^{\text{nat}}\text{Y}$ and separation by SLX and LLX. *J. Radioanal. Nucl. Chem.* **281**, 663 (2009).
19. <http://www.nndc.bnl.gov/nudat2/> (dated 3 July 2014).
20. Tarasov, O. B., Bazin, D.: Development of the program LISE: application to fusion-evaporation. *Nucl. Instrum. Meth. Phys. Res. B* **204**, 174 (2003).
21. Lahiri, S., Mukhopadhyay, B., Das, N. R.: Simultaneous production of ^{89}Zr and $^{90,91\text{m},92\text{m}}\text{Nb}$ in α -particle activated yttrium and their subsequent separation by HDEHP. *Appl. Radiat. Isotopes* **48**, 883 (1997).
22. Orysyk, S. I., Rybachuk, L. N., Pekhnyo, V. I., Korduban, A. M., Buslaeva, T. M.: The formation of Ru(III) and Rh(III) chloro aqua complexes and tautomeric forms of carboxylic acid benzoylhydrazones for the synthesis of new coordination compounds promising for the practical use. *Russian, J. Inorg. Chem.* **55**, 1075 (2010).
23. Greenwood, N. N., Earnshaw, A.: *Chemistry of the Elements*. Pergamon Press, Oxford (1989), pp. 1242–1289.