Production and separation of ^{97}Ru from ^{7}Li activated natural niobium

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Summary. The proton rich ^{97}Ru, a potential candidate for nuclear medicine, was produced for the first time through the ^{nat}Nb(^{7}Li, $3n$)^{97}Ru reaction. A natural Nb foil of 20 mg/cm^2 thickness was irradiated with 32 MeV ^{7}Li beams to attain the yield of ~ 1 MBq/μA h for ^{97}Ru. The no-carrier-added ^{97}Ru was separated from the bulk niobium by liquid–liquid extraction (LLX) and solid–liquid extraction (SLX) techniques. Liquid cation exchanger, di-(2-ethylhexyl)phosphoric acid (HDEHP) dissolved in cyclohexane was used in LLX and solid cation exchanger, DOWEX-50 was used for SLX in HCl. The LLX technique was found to be superior to the SLX technique with respect to radiochemical yield and purity of the radionuclide ^{97}Ru.

1. Introduction

Proton rich ^{97}Ru ($T_{1/2} = 2.83$ d) is a potential candidate in the field of nuclear medicine. ^{97}Ru decays to ^{97}Tc *via* EC decay mode and emits only two intense γ-lines corresponding to 215.70 keV (85.62%) and 324.49 keV (10.79%) energy. Being a member of group VIII transition metal, ruthenium has several oxidation states, the most common are Ru(II), Ru(III), Ru(IV) and Ru(VIII), which exhibit rich chemistry of Ru-complexes. The combination of excellent physical and high chemical reactivity of ^{97}Ru made it appealing for labelling compounds for delayed studies in diagnostic as well as therapeutic applications [1, 2]. It has also been observed that in some cases ^{97}Ru-labelled compound offers better results than that labelled with ^{99m}Tc or ^{111}In [3].

Among the various applications, the ^{97}Ru-PIPIDA, where PIPIDA is the anion of N-α-(p-isopropyl-acetanilide)imino-acetic acid, was found as a good alternative of ^{99m}Tc-PIPIDA [4]. The ^{97}Ru-bleomycin has been successfully used in diagnosis of tumours, while it also serves as a chemotherapeutic agent [5]. Som *et al.* [6] found ^{97}Ru-transferrin as an efficient agent for tumour and/or abscess localization as its uptake in tumours being at least three times higher than ^{67}Ga-citrate. These certainly indicate that if ^{97}Ru radionu-

clides are produced in large scale it would became one of those commonly used radionuclide in nuclear medicine.

The ^{97}Ru radionuclides have been produced so far either by neutron activation or by light charged particle activation like ^{nat}Rh(p, $2p5n$)^{97}Ru [7, 8], ^{nat}Ag(p, X)^{97}Ru [9, 10], ^{99}Tc(p, $3n$)^{97}Ru [11, 12], ^{95}Mo(α, $2n$)^{97}Ru [13], ^{94}Mo(α, n) ^{97}Ru [13], ^{nat}Mo(^{4}He, xn)^{97}Ru [14–17], ^{nat}Mo(^{3}He, xn) ^{97}Ru [14, 15], *etc.* The reactor produced ^{97}Ru through ^{96}Ru(n, γ)^{97}Ru reaction has limited applications for *in vivo* studies due to (i) its low specific activity, *i.e.*, it does not offer no-carrier-added (nca) product, which is desired in clinical applications (ii) it needs enriched ^{96}Ru (natural abundance is only 5.52%), which is expensive.

The ^{3}He and α-induced reactions on natural Mo target offers comparatively low production yield for nca ^{97}Ru. The impact of ^{3}He on natural Mo produces ^{95}Ru (1.65 h) and ^{97}Ru radionuclides *via* ^{nat}Mo(^{3}He, xn) reactions along with a number of Tc impurity, ^{93,94,95,96,99m}Tc, *via* ^{nat}Mo(^{3}He, pxn) reactions, while interaction of α-particle with ^{nat}Mo introduces contamination from another long lived isotope of Ru, ^{103}Ru (39.35 d). However, it appears advantageous to choose ^{3}He rather than the α-particle to produce nca ^{97}Ru from natural Mo target, since it offers comparatively better yield of ^{97}Ru and does not introduce the ^{103}Ru contamination [15]. Lagunas-Solar *et al.* [8] produced nca ^{97}Ru by bombarding 67.5 MeV proton on natural rhodium target and obtained ^{97}Ru yield of ~ 1.36 mCi/μA h at the end of bombardment (EOB). Apart from ^{97}Ru, signature of several other radionuclides (^{95,95m,96}Tc, ^{99,100,101}Pd, ^{97,97m,99,99m,100,101,101m,102}Rh) was observed in the irradiated rhodium target. Srivastava *et al.* [7] reported the production of nca ^{97}Ru (> 100 mCi/d) from proton (200 MeV) spallation of high purity rhodium foil at the Brookhaven Linac Isotope Producer. Zaitseva *et al.* [11] produced the nca ^{97}Ru by ^{99}Tc(p, $3n$)^{97}Ru reaction on metallic ^{99}Tc target of ~ 2.8–3.0 g/cm^2 thickness at the internal radiation facility of the JINR phasotron by bombarding 50 MeV proton beam of 8 μA intensity and achieved an yield of 40–50 mCi/h. The method is hardly feasible for routine use as the practical difficulty lies in the preparation of ^{99}Tc target which is the decay product of enormous amount of ^{99m}Tc radioactivity. Moreover, ^{99}Tc is a long lived radionuclide and therefore extreme care should be taken from the target preparation to its contamination in the final product.

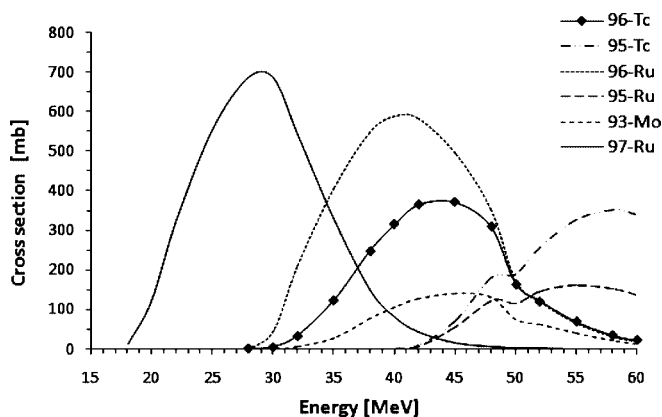* Author for correspondence (E-mail: susanta.lahiri@saha.ac.in).

Fig. 1. Theoretical excitation functions of $^7Li + ^{93}Nb$ reactions as predicted by PACE-II.

Considering the growing importance of ^{97}Ru, we have investigated a new production route of ^{97}Ru. Feasibility of the production of ^{97}Ru through $^{93}Nb(^7Li, 3n)^{97}Ru$ reaction was checked by the theoretical estimation of the excitation functions of $^7Li + ^{93}Nb$ reactions in the 15–60 MeV incident projectile energy range using the evaporation model code PACE-II [18] which is shown in Fig. 1. The theoretical calculation predicts that below 32 MeV projectile energy contaminations from other coproduced radionuclides are negligible. ^7Li reaction on ^{nat}Nb does not produce any other Ru isotopes below 40 MeV projectile energy. Therefore $^7Li +$ ^{nat}Nb reaction with appropriate projectile energy in conjunction with efficient chemistry would produce ^{97}Ru radionuclide with high radiochemical and high radioisotopic purity. These facts prompted us to go to the present investigation.

Various separation techniques have also been reported to separate the nca ^{97}Ru from the corresponding target matrix. The techniques include solvent extraction, dry distillation, coprecipitation and wet distillation methods. Srivastava *et al.* [7] achieved quantitative radiochemical separation of ^{97}Ru from the metallic rhodium foil by distillation of RuO_4 from H_2SO_4 medium in the presence of $KMnO_4$. Purification of ^{97}Ru from the natural rhodium target and coproduced Pd, Tc and Rh isotopes was reported by Lagunas-Solar *et al.* [8]. The $^{97}RuO_4$ was formed by the dissolution of activated Rh foil with 6 M HCl followed by dryness, redissolution in concentrated H_2SO_4 solution, and addition of $HClO_4$. The dissolved $^{97}RuO_4$ was then separated from the solution by distillation and was collected in ethanol. Though the ^{97}Ru-recovery efficiency in this procedure was 60–90%, the method was found to be efficient for the separation of ^{97}Ru from Pd and Rh. However, it was not found suitable for the separation of Tc isotopes as Tc isotopes are also distilled with Ru as technetium oxides, TcO_4, Tc_2O_7, *etc.* The separated ^{97}Ru in ethanol was evaporated to dryness and redissolved in HCl for the synthesis of radiopharmaceutical.

The above methods are not rapid or simple enough to be used routinely for the preparation of samples for medical use. In order to overcome the shortcomings in the previous methods, Comar and Crouzel [14] used solvent extraction technique to separate nca Ru and coproduced Tc isotopes from the α- and ^3He-activated Mo target. Ruthenium radionuclides were oxidized to RuO_4 using aqueous sodium hypochlorate solution containing 13% of active chlorine and

were extracted by carbon tetrachloride. The organic phase was evaporated to dryness adding ethylalcohol to reduce the volatility of RuO_4 and the residue was taken in 1 M HCl. They achieved radiochemical purity of ^{97}Ru was greater than 99.9%, where extraction yield ranged from 85–95%, through second time oxidation of Ru followed by extraction. In 1981, Pao *et al.* [17] proposed ion exchange techniques to separate nca ^{97}Ru from the irradiated molybdenum target. Molybdenum target was dissolved in H_2O_2 and kept into 1 M HNO_3. Active solution was then passed through the tin dioxide column followed by an anion-exchange resin column of Bio-Rad AG1-X8 in the nitrate form. The proposed method was rapid and simple resulting pure ^{97}Ru with more than 95% overall extraction efficiency. The stable molybdenum level was less than 10 μg/mL in the Ru elution peak. In 1997, Lahiri *et al.* [19, 20] produced nca $^{94,95,97,103}Ru$ along with $^{93,94,95,96,99m}Tc$ and $^{95,96}Nb$ by α-particle activation on the ^{nat}Mo target and separated nca radionuclides from the bulk ^{nat}Mo with the help of liquid–liquid extraction (LLX) using (i) anion exchanger, trioctylamine (TOA) (ii) cation exchanger, di-(2-ethylhexyl)phosphoric acid (HDEHP) and (iii) neutral liquid, tri-butyl phosphate (TBP) dissolved in cyclohexane in combination with HCl. Zaitseva *et al.* [11] separated nca ^{97}Ru from ^{99}Tc by distillation forming RuO_4 from the H_2SO_4 medium in presence of KIO_4 and achieved $\sim 95\%$ radiochemical yield of ^{97}Ru.

In this paper, an attempt has been made to produce ^{97}Ru from ^7Li induced reaction on natural niobium and the subsequent separation of nca ^{97}Ru from bulk niobium by LLX and solid–liquid extraction (SLX) techniques. HDEHP dissolved in cyclohexane and Dowex-50 have been chosen as cation exchanger for LLX and SLX techniques respectively. In SLX, no organic solvent is used and therefore is preferable if the same level of separation, purity and chemical yield are achieved. This is the first report on separation of nca Ru from bulk niobium target.

2. Experimental

2.1 Production of radionuclides

The irradiation experiments were carried out at BARC-TIFR Pelletron facility, Mumbai, India. A natural niobium (^{93}Nb) foil of 99.9% purity was procured from Alfa Aesar and was used to make a self supporting foil target of 20 mg/cm^2 thickness by proper rolling. The Nb target was bombarded by 32 MeV $^7Li^{3+}$ ions for 6 h up to a total charge of 985 μC. The total charge of irradiation was collected from an electron suppressed Faraday cup stationed at the rear of the target assembly. The residual products recoiling in the beam direction, if any, were completely stopped in the aluminum catcher foils.

Nb radionuclides required to monitor the fate of bulk target matrix in radiochemical separation, are hardly produced in the above reaction. Therefore a natural Zr foil (99.94%) procured from Johnson, Matthey & Co. Limited, UK, was rolled to 15 mg/cm^2 thickness and was subjected to irradiation with 14.5 and 21 MeV proton beam to produce ^{90}Nb (14.6 h) and ^{89}Zr (78.4 h) radioisotopes in the matrix.

After the irradiation experiment, the foils were assayed off line for the γ-ray activity of the product radionuclides by

Table 1. Nuclear spectroscopic data [21–24] of the radionuclides of interest.

Product	Nuclear reaction	Q value (MeV)	E_{th} (MeV) (calculated)	$T_{1/2}$	E_γ (keV)	I_γ (%)
^{97}Ru [21]	^{7}Li, 3n	−10.401	11.187	2.83 d	215.70	85.62
					324.49	10.79
^{96m}Tc [22]	^{7}Li, p3n	−17.985	19.344	51.5 min	778.22	1.9
					1200.15	1.1
^{96}Tc [22]		−17.585	19.344	4.28 d	778.22	99.76
					812.54	82
					849.86	98
^{95}Tc [23]	^{7}Li, p4n	−25.857	27.810	20 h	765.789	93.8
^{93m}Mo [24]	Partial nucleon exchange			6.85 h	263.062	56.7
					684.672	99.7

an HPGe detector, having 2.13 keV resolution at 1332 keV coupled with a PC based MCA, PCA2 (OXFORD). Efficiency calibration of the detector was performed as a function of γ-ray energy using a standard ^{152}Eu (13.506 y) source of known activity. Nuclear spectroscopic data of the radionuclides studied are listed in Table 1 [21–24].

2.2 Radiochemical separation

The ^{7}Li activated ^{nat}Nb foil and the proton activated ^{nat}Zr foil were separately dissolved in minimum volume of aqua regia. Nca ^{90}Nb was separated from the Zr matrix by LLX as reported in our earlier work [25]. Nca ^{90}Nb was extracted from aqueous phase of 8 M HCl into organic phase of 0.01 M TOA dissolved in cyclohexane. The recovery of nca ^{90}Nb from the organic phase was done using 10^{-3} M HCl. The ^{7}Li activated ^{93}Nb foil solution was spiked with the ^{90}Nb tracers and evaporated to dryness in order to attain the same chemical form for both radioactive ^{90}Nb tracer and bulk Nb. The residue was then redissolved into 0.01 M HCl to prepare the stock solution including ruthenium and niobium uniformly.

Separation of nca ^{97}Ru from bulk niobium was approached by LLX as well as SLX technique. A series of LLX was carried out using the cation extracting agent HDEHP dissolved in cyclohexane as organic phase and HCl as aqueous phase. In each extraction, 3 mL of organic solution was shaken with equal volume of aqueous HCl and 100 μL from the stock solution dissolved in the previous paragraph and was left for the complete phase separation. In order to determine the distribution of activities, 2 mL of aliquot was collected from each phase to carry out γ-spectrometric determination of the radionuclides. In the extraction procedure, concentration of HCl was varied keeping the HDEHP concentration fixed to 1% and the concentration of HDEHP was varied with respect to fixed 0.1 M HCl. Another set of extraction was carried out varying concentration of HDEHP with respect to the ammoniacal aqueous solution at pH 10. Nca Ru was recovered from the organic phase by using 8 M HCl.

Solid–liquid extraction has also been employed to separate nca Ru from bulk niobium using cation exchanger resin, DOWEX-50-8X (SIGMA) with different HCl media. In each extraction, 0.5 g of resin was conditioned in 10 min mixing with 3 mL HCl of each concentration. After

conditioning, 100 μL from the radioactive stock solution was added in the resin mixture and was shaken for 10 min. Supernatant was separated by centrifugation ($\sim$ 2500 rpm). The distributions of nca Ru, Tc and bulk Nb between the supernatant and the resin were measured. All the chemicals used for the chemical separation were of analytical grade.

3. Results and discussion

A non-destructive analysis of γ-spectrum ensures the production of nca ^{97}Ru along with minute amount of ^{95,96}Tc, ^{93m}Mo in the Nb target matrix. Fig. 2 represents the γ-spectrum of ^{7}Li activated natural niobium target. The batch yield of nca ^{97}Ru, ^{95,96}Tc and ^{93m}Mo has been tabulated in Table 2. Compound nuclear reaction plays the key role in the production of ^{97}Ru in the selected projectile energy range.
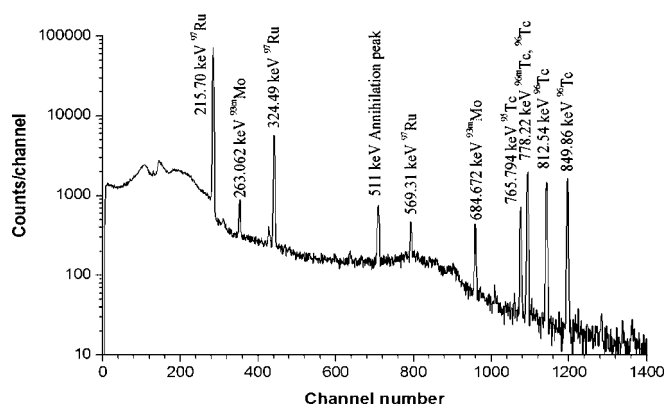
Fig. 2. Nondestructive γ-spectrum of the ^{7}Li activated natural Nb foil after 2 h of the end of bombardment.

Table 2. Batch yield of radionuclides in the experimental condition.

Experimental condition		Batch yield at EOB	
		Radioisotope	Yield (MBq/μA h)
Beam	^{7}Li^{+3} (32 MeV)	^{97}Ru (2.83 d)	1.02
Target	^{93}Nb foil (20 mg/cm^2)	^{96}Tc (4.28 d)	0.07
Dose	986 μC	^{95}Tc (20 h)	0.03
		^{93m}Mo (6.85 h)	0.01

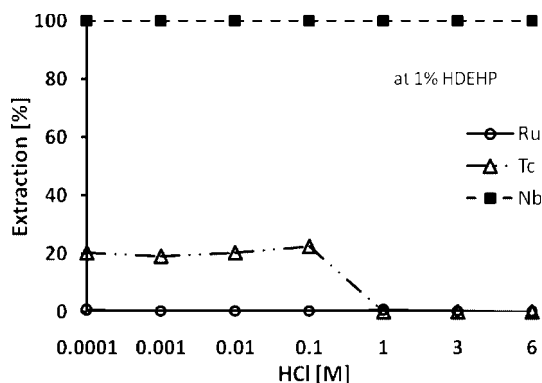**Fig. 3.** Extraction profile of nca Ru, Tc and bulk Nb in LLX as a function of HCl concentration at a fixed strength of HDEHP (1%).

Fig. 5. Extraction profile of nca Ru, Tc in LLX against varying concentration of HDEHP at pH 10.

The route $^{93}Nb(^7Li, 3n)^{97}Ru$ opens up the possibility of producing high purity nca ^{97}Ru in thick target reaction. Due to the extreme low yield and short half life of ^{93m}Mo, its signature was not observed during the radiochemical separation.

Fig. 3 represents the extraction behavior of nca Ru, Tc and bulk Nb as a function of concentration of HCl at a fixed concentration of HDEHP (1%). Bulk Nb was extracted quantitatively into the HDEHP phase and nca Ru quantitatively retained in the aqueous phase irrespective of HCl concentration. The best separation was achieved at pH 1, where 22% nca Tc was extracted into the HDEHP phase along with the bulk Nb. Another set of extraction was carried out varying concentration of HDEHP with a fixed 0.1 M HCl (Fig. 4). It was found that the best separation of bulk Nb occurs at the 10% HDEHP, where nca Ru and Tc stay quantitatively in the aqueous solution. Hence, 10% HDEHP and 0.1 M HCl revealed as the optimal condition of separation of nca Ru and Tc from the bulk Nb. Probably, niobium forms cationic species, such as $Nb(OH)_4^+$, $Nb(OH)_2Cl^{2+}$, $Nb(OH)Cl_3^+$ [26] in HCl and is thereby extracted to the HDEHP phase as found both in Figs. 3 and 4. The nca Ru stays quantitatively in the acidic medium forming neutral or anionic species along with the coproduced nca Tc. A high separation factor (D_{Nb}/D_{Ru}) of 5.5×10^7 was achieved at 0.1 M HCl and 10% HDEHP. The acidic aqueous phase was transformed to alkaline (pH 10) and LLX was performed with varying concentration of HDEHP. Fig. 5 shows the extraction profile of nca Ru and Tc at pH 10 with respect to various strengths of HDEHP. About 92% nca Ru was extracted to 0.1% HDEHP leaving nca Tc in the alkaline solu-
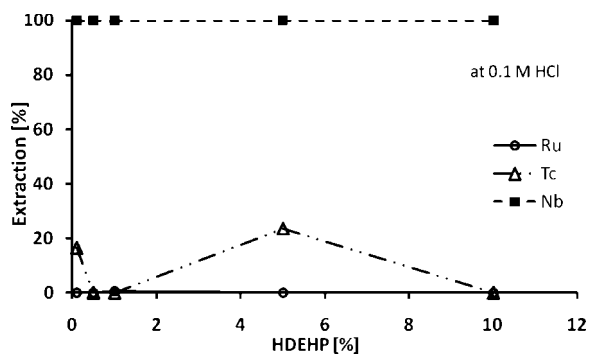
tion quantitatively. Ruthenium perhaps forms cationic complex, like $[Ru(NH_3)_6]^{2+}$ [27], in ammoniacal solution and is thereby extracted to the HDEHP phase. A separation factor (D_{Ru}/D_{Tc}) of 2×10^3 was achieved at the experimental condition. Nca Ru was then recovered from the organic phase by 8 M HCl. A schematic diagram of the production and separation of nca Ru from bulk niobium is presented in Fig. 6. This figure depicts a useful procedure for separation of ^{97}Ru from bulk Nb target using 0.1 M HCl and 10% HDEHP as aqueous and organic phases, respectively. To decontaminate from the co-produced $^{95,96}Tc$, a second extraction is necessary at alkaline pH using 0.1% HDEHP wherein nca ^{97}Ru is extracted in the organic phase which is eventually back extracted in 8 M HCl.

Fig. 4. Extraction profile of nca Ru, Tc and bulk Nb in LLX as a function of HDEHP concentration at a fixed strength of HCl (0.1 M).

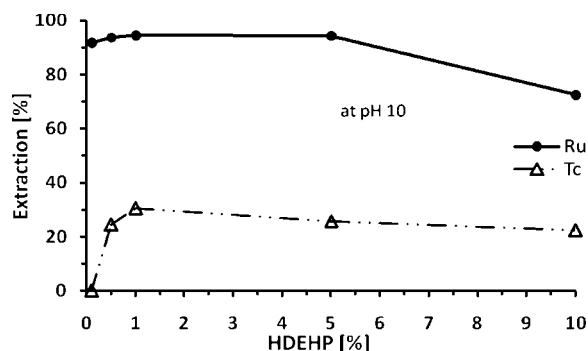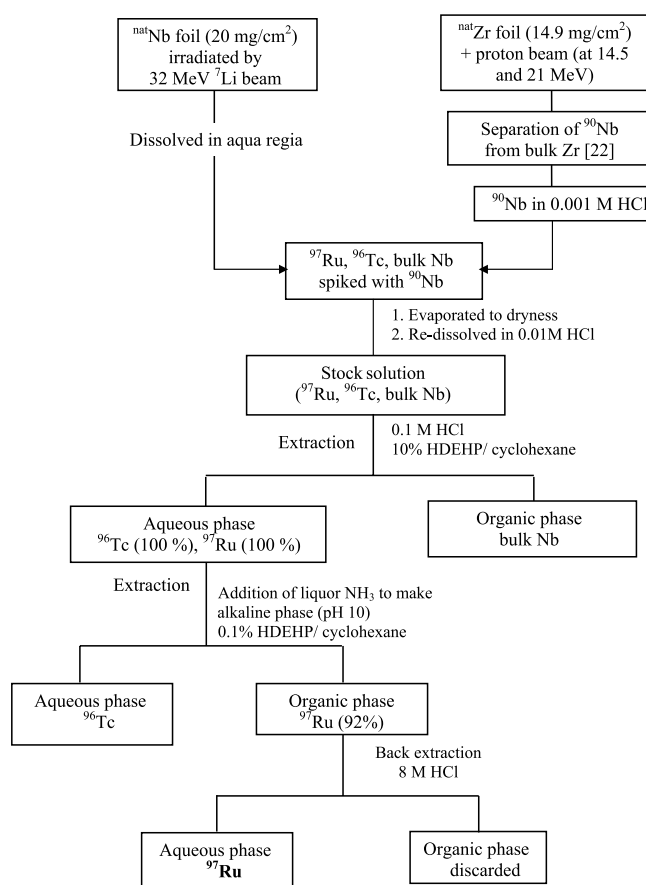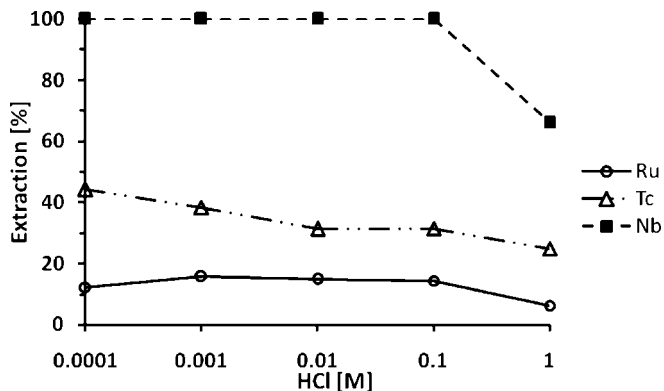**Fig. 6.** Schematics of the separation of nca ^{97}Ru and Tc from natural niobium using LLX.

Table 3. Distribution ratios (D) and corresponding separation factors (SF) of Ru and Nb on the optimal experimental conditions.

Experimental condition	D_{Nb}	D_{Ru}	SF ($= D_{Nb}/D_{Ru}$)
LLX: HCl (0.1 M)/HDEHP (10%)	1425	2.6×10^{-5}	5.5×10^{7}
SLX: HCl (1×10^{-4} M)/DOWEX-50 (0.5 g)	1153	0.14	8.24×10^{3}

Fig. 7. Extraction profile of nca Ru, Tc and bulk Nb in DOWEX-50 at varying concentration of HCl.

The separation profile of nca Ru, Tc and bulk Nb in solid–liquid extraction using cation exchanger resin DOWEX-50-8X in varying HCl medium is presented in Fig. 7. Quantitative extraction of bulk Nb has been observed in the resin phase at HCl concentrations from 1.0×10^{-4} to 1.0×10^{-1} M leaving nca Ru and Tc in the aqueous phase. Under the optimum separation condition, at 1.0×10^{-4} M HCl, about 12% of Ru and $\sim 40\%$ Tc was also extracted to the resin phase which gives a separation factor (D_{Nb}/D_{Ru}) of 8.24×10^{3}. Distribution ratios and separation factors under the best experimental condition are presented in Table 3 for both the separation techniques used in the present study.

Both the techniques employed in the present study certainly reveal the formation of same type of complexes of the bulk Nb and the nca products under the experimental condition. The total time required for the purification of nca ^{97}Ru is less than 3 h after the end of bombardment, which is essentially very small relative to the method of ^{97}Ru purification reported so far. The present production methodology includes minute production of radionuclide impurity ^{95,96}Tc, which has been efficiently removed from nca ^{97}Ru in the developed radiochemical separation techniques. Alternatively, it may be possible to suppress the production of Tc and Mo isotopes choosing the energy of the incident projectile below 30 MeV as there is no prevalent reaction channel observed in the PACE-II production below ≤ 30 MeV.

4. Conclusion

Our report introduces a new route of producing ^{97}Ru of very high radiochemical purity from ^{7}Li activation on natural niobium target. The measured batch yield of ^{97}Ru is comparable to that produced by α or ^{3}He induced reaction on natural molybdenum target. Chemical separation techniques explored to separate nca Ru from target matrix (Nb) and co-

produced nca Tc are simple, fast and reliable. In both the cases high separation factor was achieved. However, the radiochemical yield of ^{97}Ru is slightly higher in LLX (92%) compared to the SLX (88%) technique. Moreover, in SLX, ^{97}Ru fraction is accompanied by co-produced nca Tc radionuclides. The theoretical estimation suggests that the production of pure ^{97}Ru may be possible from the ^{93}Nb(^{7}Li, $3n$) reaction below 30 MeV incident projectile energy compromising with the yield of ^{97}Ru. In this case also, LLX would be the superior technique compared to SLX with respect to radiochemical yield of ^{97}Ru (100% for LLX, 88% for SLX) and radiochemical purity as revealed from the corresponding D values.

References

1. Srivastava, S. C., Richards, P., Meiken, G. E., Larson, S. M., Grunbaum, Z.: In: *Radiopharmaceuticals – Structure – Activity Relationships.* (Spencer, R. P., ed.) Grune & Stratton, New York (1981), p. 207.
2. Zoghbi, S. S., Thakur, M. L., Gottschalk, A., Pande, S., Srivastava, S. C., Richards, P.: Investigations into agents for improving cell labeling with positron and gamma-emitting radionuclides. J. Labelled Compd. Radiopharm. **18**, 280 (1981).
3. Oster, Z. H., Som, P., Gil, M. C., Fairchild, R. G., Goldman, A. G., Schachner, E. R., Sacker, D. F., Atkins, H. L., Brill, A. B.: Ruthenium-97 DTPA: A new radiopharmaceutical for cisternography. J. Nucl. Med. **22**, 269 (1981).
4. Schachner, E. R., Gil, M. C., Atkins, H. L., Som, P., Srivastava, S. C., Badia, J., Sacker, D. F., Fairchild, R. G., Richards, P.: Ruthenium-97 hepatobiliary agents for delayed studies of the biliary track I: Ru-97 PIPIDA: concise communication. J. Nucl. Med. **22**, 352 (1981).
5. 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).
6. Som, P., Oster, Z. H., Matsui, K., Guglielmi, G., Persson, B. R. R., Pellettieri, M. L., Srivastava, S. C., Richards, P., Atkins, H. L., Brill, A. B.: ^{97}Ru-transferrin uptake in tumor and abscess. Eur. J. Nucl. Med. **8**, 491 (1983).
7. 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).
8. 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).
9. Kofstad, K.: Spallation and fission of silver. Lawrence Berkeley Nat. Lab. Rep. UCRL-2265 (1953).

10. Uddin, M. S., Hagiwara, M., Baba, M., Tárkányi, F., Ditroi, F.: Experimental studies on excitation functions of the proton-induced activation reactions on silver. Appl. Radiat. Isot. **62**, 533 (2005).

11. 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}Tc$(p, 3n)^{97}$Ru reaction. Appl. Radiat. Isot. **47** 145 (1996).

12. 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}Tc$(p, 3n)^{97}$Ru reaction in 20–100 MeV proton energy range. Radiochim. Acta **56**, 59 (1992).

13. Graf, H. P., Munzel, H.: Excitation functions for α-particle reactions with molybdenum isotopes. J. Inorg. Nucl. Chem. **36**, 3647 (1974).

14. Comar, D., Crouzel, C.: Ruthenium-97 preparation with a compact cyclotron. Radiochem. Radioanal. Lett. **27**, 307 (1976).

15. Comparetto, G., Qaim, S. M.: A comparative study of production of short-lived neutron deficient isotopes ^{94,95,97}Ru in α- and ^{3}He-particle induced nuclear reactions on natural molybdenum. Radiochim. Acta **27**, 177 (1980).

16. Ramamoorthy, N., Das, M. K., Sarkar, B. R., Mani, R. S.: Studies on the production of ^{97}Ru, ^{38}K and ^{34m}Cl at the variable energy cyclotron of Bhabha Atomic Research Centre, Calcutta. In: Radiopharmaceuticals and Labelled Compounds. Proc. Int. Conf., 22–26 October 1984, Tokyo, IAEA, Vienna (1985).

17. Pao, P. J., Zhou, J. L., Silvester, D. J., Waters, S. L.: A rapid and simple separation of ^{97}Ru from irradiated molybdenum. Radiochem. Radioanal. Lett. **46**, 21 (1981).

18. Gavron, A.: Statistical model calculations in heavy ion reactions. Phys Rev. C **21**, 230 (1980).

19. Lahiri, S., Mukhopadhyay, B., Das, N. R.: LLX separation of carrier-free ^{94,95,97,103}Ru, ^{93,94,95,96,99m}Tc and ^{95,96}Nb produced in alpha-particle activated molybdenum by TOA. J. Radioanal. Nucl. Chem. **221**, 167 (1997).

20. Lahiri, S., Mukhopadhyay, B.: Liquid–liquid extraction of carrier-free radioisotopes produced in α-particle activated molybdenum target by HDEHP and TBP. Appl. Radiat. Isot. **48**, 925 (1997).

21. Nica, N.: Nucl. Data Sheets **111**, 525 (2010).

22. Abriola, D., Sonzogni, A. A.: Nucl. Data Sheets **109**, 2501 (2008).

23. Burrows, T. W., Nucl. Data Sheets **68**, 635 (1993).

24. Baglin, C. M.: Nucl. Data Sheets **80**, 1 (1997).

25. Maiti, M., Lahiri, S.: Separation of no-carrier-added ^{90}Nb from proton induced natural zirconium target. J. Radioanal. Nucl. Chem. **283**, 637 (2010).

26. Kubica, B., Tuteja-Krysa, M., Godunowa, H., Szeglowski, Z.: Adsorption of Hf and Nb on copper and zinc hexacyanoferrate(II) from HCl and H_2SO_4 solutions. J. Radioanal. Nucl. Chem. **247**, 535 (2001).

27. Greenwood, N. N., Earnshaw, A.: *Chemistry of the Elements*. Pergamon Press, Oxford (1989), pp. 1242–1289.