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Aqueous Biphasic Separation of ^{97}Ru and ^{95,96}Tc from Yttrium

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Aqueous biphasic separation technique has been attempted for the separation of ^{97}Ru, a potential candidate radionuclide in nuclear medicine, from its target matrix yttrium. Extraction of ruthenium and technetium from bulk yttrium has been carried out with 50% (w/v) PEG-4000 and PEG-6000 against 2 M solution of various salts like Na-citrate, Na-tartarate, Na-malonate, Na_2CO_3, $NaHSO_3$, Na_2SO_4, $Na_2S_2O_3$, K_2HPO_4, K_3PO_4, $(NH_4)_2SO_4$and 4 M KOH at room temperature. Influence of pH of some salt rich phases (e.g., Na-tartarate, $(NH_4)_2SO_4$) on the extraction behavior of ^{97}Ru and ^{95,96}Tc into the PEG rich phase was also studied. In presence of Na-tartarate, Na-citrate, K_2HPO_4, K_3PO_4, KOH, Na_2CO_3, Na_2SO_4, Na_2SO_3 and $(NH_4)_2SO_4$ salt solutions, preferential extraction of ^{97}Ru along with ^{95,96}Tc was obtained into the PEG rich phase. In 50% (w/v) PEG-4000-2 M $(NH4)_2SO_4$ ABS system, 83% of ^{97}Ru along with 96% of ^{95,96}Tc were extracted into PEG rich phase without any contamination of yttrium target. Back extraction of ^{97}Ru into salt rich phases from PEG rich phase was also carried out using 2 M salt solutions of K_2CO_3, $Na_2S_2O_3$ and 4 M KOH. About 90% back extraction of ^{97}Ru into salt rich phases without any contamination of ^{95,96}Tc was obtained with 2 M $Na_2S_2O_3$ salt solution. Dialysis study of PEG rich phase containing ^{97}Ru along with ^{95,96}Tc was also carried out against deionised water to obtain pure ^{97}Ru.

Introduction

Polyethylene glycol (PEG) based aqueous biphasic systems (ABS) is greener analytical technique compared to traditional solvent extraction system, as both the phases in ABS are aqueous in nature [1]. ABS can be formulated with water-soluble polymer PEG and other polymers with one another or PEG with inorganic salts like sulphate, phosphate, carbonate, etc., in particular concentrations [2]. Properties of ABS generally depend on the phase components of the ABS system. PEG can be chosen as one of the phase forming components because of its nontoxic, non-flammable, and inexpensive nature [3-5]. In addition, PEG rich phase in PEG-ABS system is tunable and therefore, their phase characteristics can be modified by fine tuning of PEG rich phase for better partitioning behavior of solute into the PEG rich phase.

Various applications of ABS systems in the field of separation, purification of organic molecules, metal ions were reported in literature. Roger *et al.* reported partitioning behavior of pertechnetate using PEG-ABS system [3, 5-6]. For about last ten years, our laboratory made continuous endeavor to develop new green separation methodologies, using aqueous biphasic system [7-16] or other environmentally benign reagents like polyvinylpyrrolidone [17-18], ionic liquids [19], etc.

In this paper we made an attempt to separate Ru and Tc radionuclides from bulk yttrium target. The radiometric methods were employed for detection. The corresponding radioisotope like ^{97}Ru, ^{95,96}Tc and ^{88}Y were used as precursor of Ru, Tc and Y respectively. The motivation of the experiment lies in the fact that ^{97}Ru is a candidate radionuclide in nuclear medicine which may have potential application in diagnostic imaging as well as for the therapeutic purpose because of its suitable chemical and nuclear properties such as moderate half life ($T_{1/2}$: 2.83 d) and high intensity low energy γ rays (216 keV, 86% and 324.5 keV, 10.25%). Due to presence of multiple oxidation states such as Ru(II), Ru(III), Ru(IV) and Ru(VIII) and various coordination numbers (4, 5 & 6); Ru can form series of complexes, which have useful properties to tune various metal-ligand combination for radiopharmaceutical chemistry [20]. Generally, reported production routes of ^{97}Ru are by neutron, proton and alpha particle activation [21-31]. Recently, we reported two new production routes of ^{97}Ru by heavy ion activation such as activation through ^{nat}Nb(^{7}*Li, 3n*)^{97}Ru [32] and ^{nat}Y(^{12}*C, p3n*)^{97}Ru reactions [33]. In the last reaction, i.e., bombarding yttrium target with high-energy ^{12}C (75 MeV), ^{97}Ru and ^{95,96}Tc are produced in the target matrix.

The separation of ^{97}Ru from the corresponding targets were reported using different analytical techniques such as solvent extraction, dry distillation, co-precipitation, wet distillation, liquid-liquid extraction and solid-liquid extraction methods. Separation of ^{97}Ru from Tc, Rh targets using distillation technique based on distillation of $^{97}RuO_4$ in concentrated HNO_3 or H_2SO_4 medium at 90^oC was reported in literature with a total separation time of 6-7 h [21-22, 25]. Comar *et al*. developed and claimed simple and rapid solvent extraction process compared to distillation process for the separation of Ru and co-produced Tc radionuclides from molybdenum target [28]. Tin dioxide column followed by an anion exchange column was employed for the separation of ^{97}Ru from bulk molybdenum target [31]. Liquid–liquid extraction (LLX) using liquid anion exchanger trioctylamine (TOA) or liquid cation exchanger as di-(2-ethylhexyl)phosphoric acid (HDEHP) along with tri-butyl phosphate (TBP) was used for separation of ^{97}Ru from coproduced Tc, Nb radionuclides and bulk Mo target by Lahiri *et al*. [34-35]. Radiochemical separation of NCA ^{97}Ru from bulk Nb and coproduced Tc by both LLX using HDEHP and SLX using cation exchanger resin DOWEX-50 was exploited by Maiti *et al* [32]. Maiti *et al* also reported the separation of ^{97}Ru and coproduced ^{95}Tc from bulk yttrium target by LLX using TOA [33]. Recently, we have developed PEG based aqueous biphasic system for separation of

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^{97}Ru from bulk niobium target [12]. We also developed method of separation of ^{97}Ru from ^{12}C induced natural yttrium target by ion exchange resins [36]. In this paper, we have made an attempt to develop another green method for separation of ^{97}Ru from ^{12}C induced bulk Y target and co-produced $^{95,96}Tc$ using PEG based ABS system.

Material and Methods

Irradiation: Dictated by the theoretical calculation [33], we bombarded natural Y foil (99.9% purity, Alfa Aesar) with 75 MeV of $^{12}C^{6+}$beam for 14 h at BARC-TIFR Pelletron facility, Mumbai for the production of ^{97}Ru and $^{95,96}Tc$ [33, 37]. Bulk Y target was monitored radiometrically using ^{88}Y. Gamma-spectroscopic measurements were carried out using HPGe (CANNBERA) detector of 2.7 keV resolution at 1332 keV. After the end of bombardment (EOB), the ^{12}C irradiated ^{nat}Y target was cooled for 50 h to allow the decay of all short-lived products. The carbon irradiated ^{nat}Y foil was dissolved in minimum volume of 0.1 M HCl and was spiked with ^{88}Y, evaporated to dryness, re-dissolved in 0.01 M HCl to prepare the stock solution containing ^{97}Ru, $^{95,96}Tc$ and ^{88}Y along with bulk Y.

Materials and Procedure: The chemicals such as PEG-4000, PEG-6000, HNO_3, HCl, HF and the salts such as Na-citrate, Na-tartarate, Na-malonate, $(NH_4)_2SO_4$, $NaHSO_3$, Na_2SO_4, Na_2SO_3, $Na_2S_2O_3$, K_2HPO_4, K_3PO_4, Na_2CO_3, and KOH were obtained from Merck, India. All reagents were of analytical grade. The dialysis sack was procured from Spectrum Laboratory Inc.

Molecular weight and concentration of PEG, salt concentration and type of salts employed are the important parameters to obtain maximum phase separation in ABS systems. PEG-4000 with 50% (w/v) concentration is reported as an optimum condition to minimize the solubility of any salt rich phase in the polymer rich phase [9, 38]. Also it has been found that 2-4 M salt concentration is ideal to obtain maximum phase separation. In the present work, therefore, 50% (w/v) PEG-4000 solution and 2 M salt solutions of Na-citrate, Na-tartarate, Na-malonate, $(NH_4)_2SO_4$, $NaHSO_3$, Na_2SO_4, Na_2SO_3, $Na_2S_2O_3$ K_2HPO_4, K_3PO_4, Na_2CO_3, and 4 M KOH were prepared by dissolving appropriate quantity in deionized water. In case of PEG-6000, optimum concentration of PEG rich phase was also observed as 50% (w/v) as solubility of any salt rich phase in the PEG rich phase was minimum at this concentration. Therefore throughout the experiment 50% (w/v) of PEG-4000 and PEG-6000 was employed. In many of our earlier experiments, it has been found that lower molecular weight PEGs like PEG-400 or PEG-600 are not suitable for metal separation studies. This is because these polymers are like wool balls whose complexing-end becomes difficult to identify [10]. Similarly we have seen that PEG-20000 is also not so effective in separating metal ions [12]. Therefore, the extraction studies were performed with 3 mL of 2 M various salt solutions with equal volume of 50% (w/v) of PEG-4000 as well as PEG-6000 solutions. 0.2 mL stock solution containing ^{97}Ru, $^{95,96}Tc$ and bulk yttrium spiked with ^{88}Y was added to this system and was shaken for 10 min. Then system was kept for 10 min to achieve phase separation before collecting 2 mL of each phase for the γ-spectroscopic studies. Chemical separations were carried out at room temperature. The effect of pH and efficiency of PEG-6000 over PEG-4000 were also studied.

Back extraction of ^{97}Ru and $^{95,96}Tc$ into the salt rich phases from PEG rich phase was carried out using 2 M salt solutions such as K_2CO_3, $Na_2S_2O_3$ and 4 M KOH. Dialysis study was performed using suitable length of Dialysis membrane sack (Molecular weight cut off 1000 Dalton, wet in 0.1% Na-azide), against deionized water on a low speed mechanical shaker to obtain pure NCA ^{97}Ru in aqueous medium .

Results and Discussion

The extraction patterns of ^{97}Ru, $^{95,96}Tc$ and bulk Y in PEG-rich phase against different salt-rich phases [Fig.1] shows preferential extraction of ^{97}Ru and $^{95,96}Tc$ into the PEG phase in all 12 salts-PEG combinations. Ru along with Tc radionuclides were extracted to the PEG rich phase without any contamination of bulk yttrium when Na-tartarate, Na-citrate, K_2HPO_4, K_3PO_4, KOH, Na_2CO_3, Na_2SO_4, Na_2SO_3 and $(NH_4)_2SO_4$ were used as salt solutions. This could be due to strong complexation of yttrium with citrate, tartarate, HPO_4^{-2}, PO_4^{-3} CO_3^{-2}, SO_4^{-2} and SO_3^{-2} and bulk Y prefer to stay in the salt rich phase whereas complexing ability of Ru and Tc with these salts was less due to larger size and were extracted into the PEG phase. Generally, Ru is present as ruthante (RuO_4^{-2}; calculated ionic radius~ 180 pm, [39]) and Tc is present as pertechnate (TcO_4^{-}, ionic radii: 206 pm) whereas yttrium is present as free Y^{+3}(ionic radii: 89 pm, [40]). Therefore, preferential extraction of ^{97}Ru and $^{95,96}Tc$ into the PEG phase could be due to the larger size of Ru and Tc compared to the Y. Usually, ions with smaller ionic radii are more solvated and prefer to stay in the salt rich phase whereas larger size cations act like hydrophobic molecules as entropies of hydration of these ions are positive and prefer to stay in PEG rich phase. However, in three cases, e.g., when Na-malonate, $NaHSO_4$ and $Na_2S_2O_3$ were used as salt-rich phase, slight extraction of Y was also observed. Maximum extraction of ^{97}Ru and $^{95,96}Tc$ in the PEG rich phase was 83% and 96% respectively when $(NH_4)_2SO_4$ was used as salt rich phase, without any contamination of bulk yttrium.

To study the influence of molecular weight of PEG on the extraction system, the same experiment was carried out with PEG-6000 against 2 M Na-tartarate, Na-citrate, Na-malonate and K_2HPO_4 as salt rich phases. Results have been shown in Fig.2. It was observed that PEG-6000 has marginal impact on the extraction patterns of ^{97}Ru, $^{95,96}Tc$ and bulk Y over PEG-4000. Therefore, all other experiments were carried out with only PEG-4000 only.

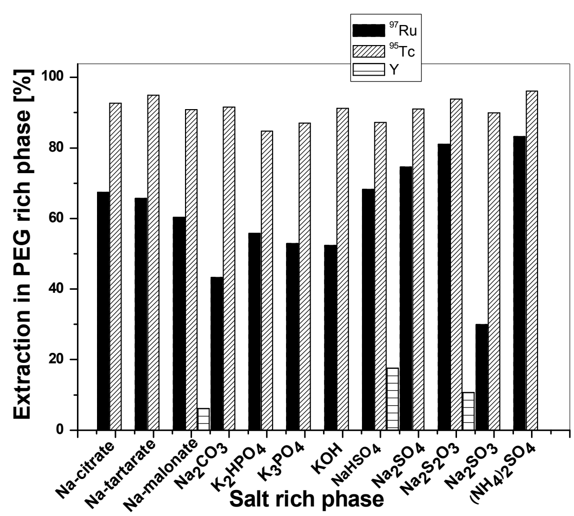

Fig-1 Extraction profile of ^{97}Ru, ^{95}Tc and bulk Y in PEG rich phase against different salt-rich phases at the natural pH of the salts at room temperature.

The Effect of pH on the extraction of ^{97}Ru, $^{95,96}Tc$ and bulk Y into the PEG rich phase was investigated by varying the pH of $(NH_4)_2SO_4$ and Na-tartarate salt solutions as salt rich phase (Fig.3 & Fig.4). The pH of the $(NH_4)_2SO_4$ and Na-tartarate salt solutions was adjusted using dilute HCl or ammonia solution before mixing with the PEG rich phase. It has been observed that the extraction patterns of the radionuclides under investigation are almost invariant on change of pH. However, the best separation was obtained at pH 5 when Na-tartarate or $(NH_4)_2SO_4$ were used as salt rich phase. For further improvement of the chemical yield of ^{97}Ru and $^{95,96}Tc$, the relative volumes of PEG-4000 and salt rich phase (2 M Na-tartarate or $(NH_4)_2SO_4$) were varied. In case of 2 M Na-tartarate, when the volume of PEG phase was doubled compared to the salt rich phase, about 78% ^{97}Ru and 100% ^{95}Tc extraction were obtained into the PEG rich phase. The higher volume of PEG rich phase offers more sites for salting out of ^{97}Ru and ^{95}Tc into the PEG rich phase. In case of $(NH_4)_2SO_4$ as salt rich phase, volume to PEG was also increased to improve the chemical yield of ^{97}Ru along with $^{95,96}Tc$. However, with increase in PEG volume, extraction of bulk yttrium along with ^{97}Ru and $^{95,96}Tc$ was observed. Distribution ratios (*D*) and separation factors (*S*) of ^{97}Ru, ^{95}Tc and yttrium in various experimental conditions were calculated and results are shown in Table 1. At typical experimental condition (PEG-4000, 2 M $(NH_4)_2SO_4$) separation factors ($S_{Ru/Y}$) and ($S_{Tc/Y}$) were as high as $4.0 \cdot 10^3$ and $2.0 \cdot 10^4$ respectively.

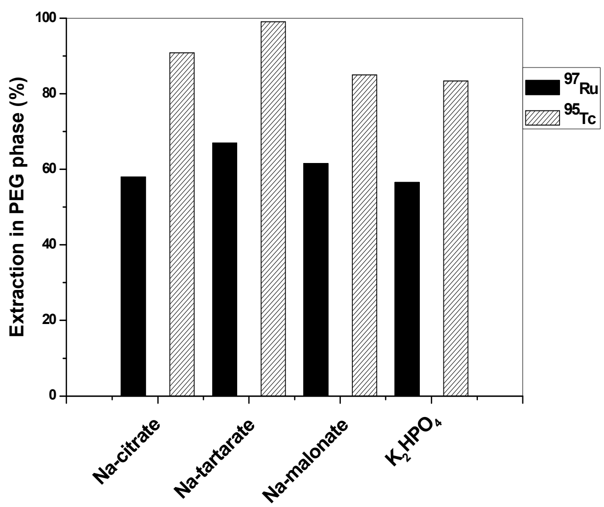

Fig-2 Extraction profile of ^{97}Ru, ^{95}Tc and bulk Y in with PEG-6000 against different salt-rich phases at the natural pH of the salts at room temperature.

Back extraction of ^{97}Ru from PEG rich phase: After removing bulk yttrium, back extraction of ^{97}Ru and $^{95,96}Tc$ into the salt rich phase from PEG rich phase was carried out using 2 M of K_2CO_3, $Na_2S_2O_3$ and 4 M of KOH as salt rich phase. With 2 M of K_2CO_3 and 4 M of KOH, 5% and 14% of ^{95}Tc was also stripped back along with 68% and 81% of ^{97}Ru respectively into the salt rich phase. However, with 2 M $Na_2S_2O_3$, about 93% stripping of ^{97}Ru into salt rich phase without any contamination of $^{95,96}Tc$ was observed [Fig.5]. This could be due to larger negative value of Gibbs free energy of hydration for pertechnate (ΔG_{hyd}:- 637 kJ/mol) compared to ruthenate (ΔG_{hyd} :- 307 kJ/mol) [41] and therefore Tc preferred to stay in the PEG rich phase.

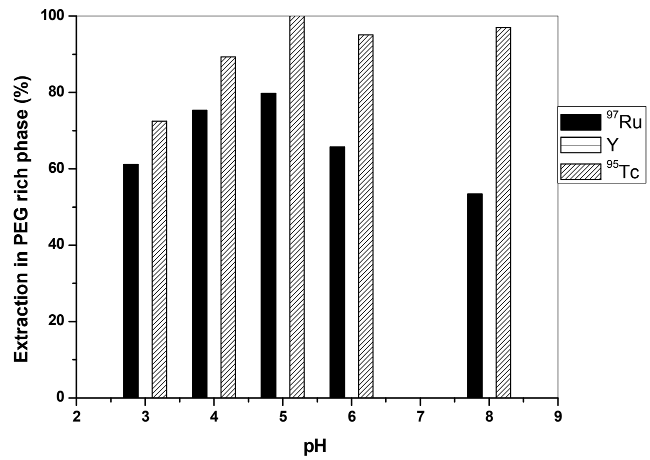

Fig-3 Extraction profile of ^{97}Ru, ^{95}Tc and bulk Y against different pH of Na-tartarate

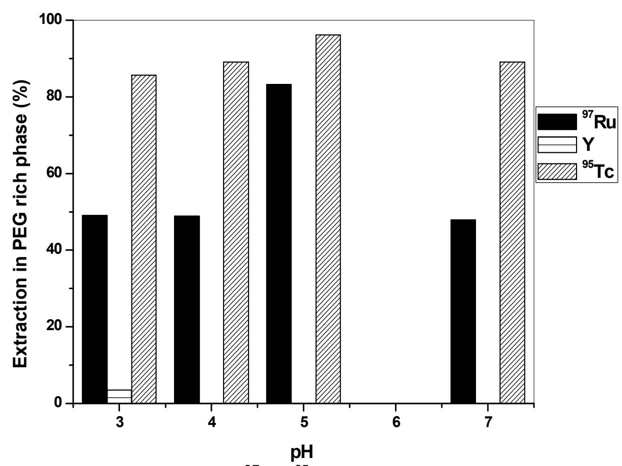

Fig-4 Extraction profile of ^{97}Ru, ^{95}Tc and bulk Y against different pH of $(NH_4)_2SO_4$.

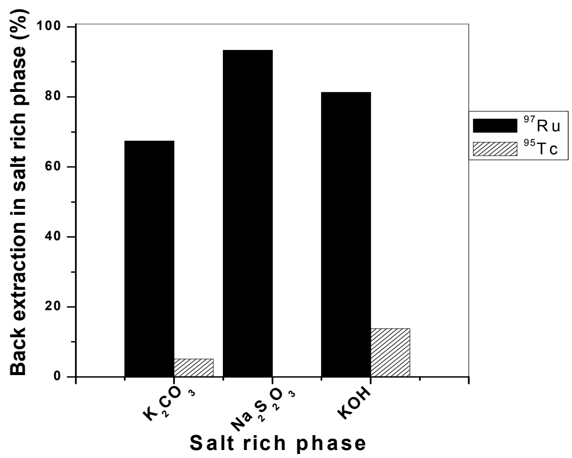

Fig-5 Back extraction profile of NCA ^{97}Ru and co-produced Tc from PEG rich phase to salt rich phase.

Table 1. Distribution ratios (*D*) and separation factors (*S*) of ^{97}Ru, ^{95}Tc and yttrium at room temperature.

Salt rich Phase (2M)	pH	PEG rich phase	Distribution ratios (*D*)			Separation factors(S)		
			D_{Ru}	D_{Y}	D_{Tc}	$S_{Ru/Y}$	$S_{Tc/Ru}$	$S_{Tc/Y}$
Na-citrate	7	4000	2.1	1.8×10^{-3}	12.7	1.1×10^{3}	6.1	7.0×10^{3}
Na-citrate	7	6000	1.4	1.2×10^{-3}	9.8	1.2×10^{3}	7.0	8.2×10^{3}
Na-tartarate	5	4000	1.9	1.1×10^{-3}	18.8	1.7×10^{3}	9.8	1.7×10^{4}
Na-tartarate (3 mL)	5	4000 (6mL)	3.5	1.4×10^{-3}	1.0	2.5×10^{3}	0.3	7.1×10^{2}
Na-tartarate	3	4000	1.6	1.4×10^{-3}	2.6	1.1×10^{3}	1.6	1.8×10^{3}
Na-tartarate	4	4000	3.0	1.4×10^{-3}	8.3	2.1×10^{3}	2.7	5.9×10^{3}
Na-tartarate	5	4000	3.9	1.4×10^{-3}	1	2.8×10^{3}	0.2	0.7×10^{3}
Na-tartarate	8	4000	1.1	1.4×10^{-3}	32.5	7.8×10^{2}	29.5	23.2×10^{3}
Na-tartarate	5	6000	2.0	1.1×10^{-3}	9.1	8.3×10^{3}	4.5	8.3×10^{3}
Na-Malonate	7	4000	1.5	6.5×10^{-2}	9.8	2.3×10^{1}	6.5	1.5×10^{2}
Na-Malonate	7	6000	1.6	1.3×10^{-3}	5.6	2.1×10^{3}	3.5	4.3×10^{3}
Na_2CO_3	11	4000	0.7	1.3×10^{-3}	10.9	5.5×10^{2}	14.3	7.9×10^{3}
K_2HPO_4	8	4000	1.3	9.7×10^{-4}	5.5	1.3×10^{3}	4.4	5.7×10^{3}
K_2HPO_4	8	6000	1.3	9.8×10^{-4}	5.0	1.3×10^{3}	3.8	5.1×10^{3}
K_3PO_4	10	4000	1.1	1.1×10^{-3}	6.7	9.8×10^{2}	9.4	5.8×10^{3}
KOH	10	4000	0.1	1.3×10^{-3}	4.3	8.9×10^{1}	3.1	3.2×10^{3}
$NaHSO_4$	5	4000	2.1	2.1×10^{-1}	6.8	1.0×10^{1}	3.4	3.2×10^{1}
Na_2SO_4	6	4000	2.9	1.3×10^{-3}	10.1	2.1×10^{3}	3.5	7.3×10^{3}
$Na_2S_2O_3$	5	4000	4.3	1.1×10^{-1}	15.2	3.6×10^{1}	20.9	1.3×10^{2}
Na_2SO_3	9	4000	0.4	1.3×10^{-3}	8.9	3.3×10^{2}	4.9	6.9×10^{4}
$(NH_4)_2SO_4$	5	4000	4.9	1.3×10^{-3}	24.8	3.9×10^{3}	6.1	1.9×10^{4}
$(NH_4)_2SO_4$	3	4000	0.9	3.7×10^{-2}	5.9	2.4×10^{1}	6.5	1.6×10^{2}
$(NH_4)_2SO_4$	4	4000	0.9	1.0×10^{-3}	8.08	9.0×10^{2}	8.9	8.1×10^{3}
$(NH_4)_2SO_4$	7	4000	0.9	1.1×10^{-3}	8.08	8.2×10^{2}	8.9	7.3×10^{3}
$(NH_4)_2SO_4$ (3 mL)	5	4000(6 mL)	5.4	1.4×10^{-3}	1.0	3.8×10^{3}	0.2	7.1×10^{2}

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3.2 Dialysis studies of ^{97}Ru containing PEG rich phase: Attempt has been made to take out ^{97}Ru into deionized water only. This experiment was carried out with back extracted ^{97}Ru fraction in $Na_2S_2O_3$ phase (Fig.5). The entire ruthenium was back extracted to the PEG-4000 phase by 10 min shaking the salt solution with 3 mL PEG-4000. Now the dialysis of the PEG rich phase was carried again in deionized water. During dialysis, the dissociated ^{97}Ru from ^{97}Ru-PEG association was continuously removed from the dialysis sack. Percentage of retention of ^{97}Ru in dialysis sack is shown in Fig.6. It was observed that after 4 h about 74% ^{97}Ru was removed from the dialysis sack. ln[^{97}Ru-PEG association] against time was also plotted to measure the half life of ^{97}Ru-PEG association [Fig.7]. The half-life of the association was found to be 5.4 h, which is good enough for the equilibration process when this complex is present inside body during therapeutic or diagnostic purpose.

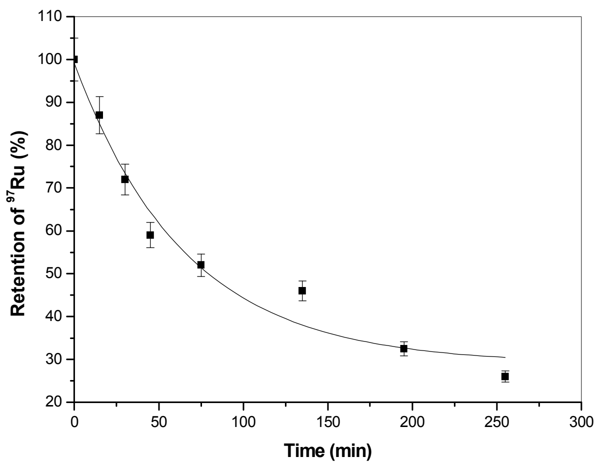

Fig-6 Retention of ^{97}Ru in dialysis sack with respect to time

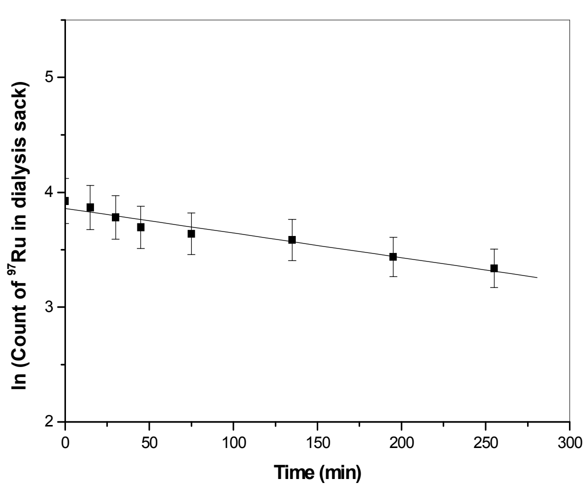

Fig-7 Plot of ln (counts of ^{97}Ru of -PEG in dialysis sack) vs. Time

Conclusions

Environmental friendly greener method was developed for the separation of Ru and Tc radionuclides from bulk yttrium using PEG based aqueous biphasic system. The method is rapid and cost-effective. Synthetic polymer like PEG is a water-soluble and is not considered as toxic. However, some applications e.g., in vivo use of ^{97}Ru, may need these radionuclides in aqueous solution only. Therefore, ^{97}Ru may be obtained in aqueous medium by dialysis of ^{97}Ru containing PEG phase. The favorable half-life of ^{97}Ru, its complexing ability, and the simplicity of the separation method we developed without using any toxic chemicals might be useful in future in the field of radiopharmaceuticals and clinical application of this radionuclide.

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