

Radiochemical purification of ^{144}Ce from its in-grown daughter ^{144}Pr and other fission products

G.V.S. Ashok Kumar, R. Kumar* and M. Joseph

Materials Chemistry and Metal Fuel Cycle Group, Indira Gandhi Centre for Atomic Research, HBNI, Kalpakkam, Tamil Nadu-603102, India.

Received August 21, 2018; Accepted December 26, 2018; Published online February 8, 2019

^{144}Ce - ^{144}Pr is one of the radionuclide generators used for demonstration of radioactive equilibrium, an important concept in radioactive decay kinetics for pedagogic activities in nuclear physics and chemistry practicals. This work describes the method of purification of ^{144}Ce from mixed oxide fuel dissolver solution of FBTR by ion-exchange chromatography using Dowex resin followed by solvent extraction using di-(2-ethylhexyl)phosphoric acid (HDEHP). The daughter nuclide ^{144}Pr was purified by extraction chromatographic technique using HDEHP coated XAD-7 resin. The purified ^{144}Ce was used to demonstrate radioactive equilibrium concept from the growth of its daughter nuclide ^{144}Pr .

1. Introduction

The phenomenon of radioactive equilibrium is described extensively in the literature [1-4]. Radioactive equilibrium is a condition in which the ratio of the parent and its daughter activities remains constant whenever the daughter's half-life is shorter than that of the parent. However, there is no possibility of achieving the equilibrium condition if the parent half-life is shorter than that of the daughter. Further, there exist two types of equilibria i.e. secular and transient. A radioactive equilibrium between the parent and the daughter is referred as either transient or secular equilibrium, depending upon the relative half-lives of the parent and daughter in a pair. For a secular equilibrium, half-life of the parent is greater than half-life of daughter by at least an order of magnitude. However for a transient equilibrium, the ratio of the half-life of the parent to that of the daughter is about or less than 10. Various parent-daughter pairs which are in radioactive equilibrium are shown in the Table 1 [5-11].

In a radioactive equilibrium, the daughter always appears to decay with the half-life of the parent as long as it is present in the mixture but decays with its own half-life when separated from its parent. This observation is explained from the fact that the daughter is continuously produced from the parent when it is in equilibrium with the latter. In the case of secular equilibrium, the activity ratio of parent to daughter tends towards a constant value i.e. unity in this case. Further, the activity of parent remains apparently constant over the period of measurement because of its relatively very long half-life in

comparison with that of daughter and hence its activity shows no significant or negligible change during the period of measurement. However, the activity of the daughter increases continuously until the rate of formation of the daughter equals to the rate of decay of the parent. Hence, the secular equilibrium phenomenon can be defined as a condition in which the ratio of activities of the parent and daughter radionuclides becomes a constant i.e. unity with no significant or observable change in the parent activity during the period of observation [4]. Similarly, the ratio in the transient equilibrium is also a constant, but less than unity depending upon the decay constants of parent and daughter nuclides.

Among them, the pair ^{144}Ce - ^{144}Pr was chosen to demonstrate the concept of radioactive equilibrium in general and secular equilibrium in particular in this work for a practical convenience even though some of the other pairs also can be used for the same. Among the known pairs which are in secular equilibrium as shown in table 1, the ^{90}Sr - ^{90}Y has the disadvantage of having relatively a long lived daughter with a half-life of 2.7 d, which demands the observation period of more than about two weeks for the convenient demonstration of the phenomenon of secular equilibrium. The other pair ^{137}Cs - $^{137\text{m}}\text{Ba}$ has a relatively short half-life for its daughter i.e. 2.55 min which is convenient to establish the secular equilibrium phenomenon in a relatively short observation time but limits the accuracy in the measurement of the half-life of the daughter nuclide owing to the practical delay between the purification of the parent nuclide and the starting of the assay of the total activity using a detector. However, the pair ^{144}Ce - ^{144}Pr which

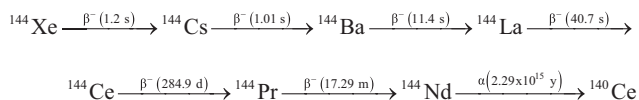
TABLE 1: Parent-Daughter pairs which are in radioactive equilibrium

| Type of equilibrium | Parent-Daughter pair | Half-life of Parent ($T_{1/2(P)}$) | Half-life of Daughter ($T_{1/2(D)}$) | Ratio $T_{1/2(P)}/T_{1/2(D)}$ |
|---------------------|---|--------------------------------------|--|-------------------------------|
| Secular | ^{137}Cs - $^{137\text{m}}\text{Ba}$ | 30 y | 2.55 min | 6.2×10^6 |
| | ^{144}Ce - ^{144}Pr | 285 d | 17.3 min | 2.37×10^4 |
| | ^{90}Sr - ^{90}Y | 28.8 y | 2.7 d | 3.9×10^2 |
| Transient | ^{99}Mo - $^{99\text{m}}\text{Tc}$ | 2.75 d | 6.0 h | 11.0 |
| | ^{166}Dy - ^{166}Ho | 3.4 d | 1.117 d | 3.04 |
| | ^{72}Se - ^{72}As | 8.4 d | 1.08 d | 7.77 |

*Corresponding author. E-mail: rkumar@igcar.gov.in

is in secular equilibrium has reasonable half-lives providing a convenient observation time of establishing the secular equilibrium phenomenon (~ 2 h) as well as the measurement of half-life accurately.

In order to profile the growth of the daughter with a better accuracy, in a demonstration experiment, it is necessary to have a pure source of the parent, ^{144}Ce , free from its in-grown daughter of ^{144}Pr in this case. The only viable source for the production of ^{144}Ce is the nuclear fission. The chain yields of the mass number 144 are 5.38% and 3.82% for the thermal neutron induced fission of ^{235}U and ^{239}Pu , respectively; but the same are 5.34%, 4.65% and 3.73% for the fast fission of ^{235}U , ^{238}U and ^{239}Pu , respectively [12]. The decay chain for the isobaric series corresponding to the mass number 144 is as follows.



The decay chain rapidly accumulates in to the long-lived ^{144}Ce . Thus, the presence of ^{144}Ce and its daughter (^{144}Pr) are the only observable radionuclides practically because of the fact that all the precursors of ^{144}Ce are short-lived. Decay schemes of ^{144}Ce and ^{144}Pr are depicted in Fig. 1 [13, 14]. The parent nuclide ^{144}Ce decays in to its daughter nuclide ^{144}Pr through β^- emission which again decays into ^{144}Nd by a beta emission. The half-lives of ^{144}Ce and ^{144}Pr are 284.9 d and 17.29 min, respectively. Some of the important decay characteristics of the parent ^{144}Ce and its daughter ^{144}Pr are shown in the Table 2.

As the daughter nuclide ^{144}Pr is short-lived, the generator would be used many times a day with the maximum activity of ^{144}Pr which allows repeated studies. The special feature of this nuclide is having well-spaced gamma photons of 696, 1489 and 2185 keV, which enables information of the depth distribution of ^{144}Pr labelled tracer in extended volumes [15]. The separated ^{144}Ce - ^{144}Pr pair is having several other applications. The purified ^{144}Ce source can be used as a radioactive tracer in chemical and biochemical application studies to track the path of cerium [16]. It can be used as energy and efficiency calibration source for the gamma spectrometric studies like HPGe detector [17]. It is also being tested as a potential candidate for the interstitial and intravascular brachytherapy applications due its relative long half-life [18, 19]. The ^{144}Ce - ^{144}Pr pair is also widely used for the demonstration of secular equilibrium to explain the radioactive equilibrium concept to students [8]. The present study deals with the usage of pure ^{144}Ce parent towards the demonstration of radioactive secular equilibrium.

To demonstrate the secular equilibrium behaviour using ^{144}Ce - ^{144}Pr , it is preferred to start with a pure parent ^{144}Ce followed by assaying it by a suitable counting technique and thus the in-growth of daughter with the parent is profiled until the equilibrium or steady state is reached. Several methods were reported for the separation of ^{144}Pr from ^{144}Ce , particularly towards the development of its radio nuclide generator [7, 8]. However, reports on the source preparation of ^{144}Ce for the demonstration of secular equilibrium concept were limited. Walter et al. [7] studied the absorption of ^{144}Ce from ^{144}Pr on manganese dioxide coated alumina and elution of ^{144}Pr under different conditions. Semmelrogge et al.[8] carried out the studies on secular equilibrium of ^{144}Ce - ^{144}Pr in which ^{144}Ce was separated by solvent extraction followed by its precipitation on a planchet. Tompkins et al. studied the separation of ^{144}Pr from ^{144}Ce using a cation-exchange resin, Dowex 50 with a 5% citrate complexing solution (pH=3.0) as the eluant [20]. But McDonald et al. [21] studied the same using an anion exchange resin, Dowex 1 (100-200), and 9 M HNO_3 containing 0.5 N NaBrO_3 as an eluant. Bradley et al. [22] separated ^{144}Ce

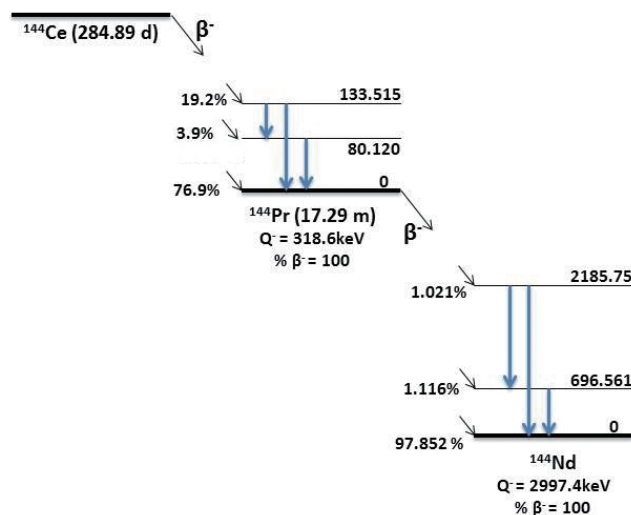


Figure 1. Decay scheme of ^{144}Ce and ^{144}Pr [13, 14].

TABLE 2: Decay characteristics of the parent and daughter

| | Gamma energy (keV) | % Intensity | β^-_{max} (keV) | % Intensity |
|-------------------|--------------------|-------------|------------------------------|-------------|
| ^{144}Ce | 133.5 | 10.83% | 185.1 | 19.2% |
| | 80.1 | 1.4% | 238.5 | 3.9% |
| | 53.4 | 0.1% | 318.6 | 76.9% |
| ^{144}Pr | 696.5 | 1.4% | 811.8 | 1.02% |
| | 1489.2 | 0.28% | 2301 | 1.12% |
| | 2185.7 | 0.73% | 2997.5 | 97.85% |

from ^{144}Pr as an insoluble iodate salt of Ce in the oxidation state +4.

All these methods describe either the separation of ^{144}Pr from ^{144}Ce , or precipitation of ^{144}Ce , a time consuming and a relatively clumsy process which is a matter of concern especially while demonstrating the secular equilibrium concept in a normal chemistry laboratory where the radiochemical processing is carried out very carefully observing all the safety precautions to avoid contamination. In order to establish the secular equilibrium and to determine the half-life of daughter nuclide, it is important to obtain a sample of parent nuclide ^{144}Ce with as much purity as possible, so that the profiling of daughter nuclide before reaching the radioactive equilibrium can be accomplished conveniently as accurately as possible. To follow the kinetics more proficiently, the time gap between the separation of ^{144}Ce and its counting should be as short as possible. Hence, a rapid solvent extraction method was demonstrated in this work in which the pure parent (^{144}Ce) was obtained and assayed very immediately after its separation. Extraction chromatographic studies were also carried out to separate pure ^{144}Pr and subsequently follow its half-life by which its purity was ascertained clearly and indirectly, for reporting its half-life unambiguously. The present work describes a simple and rapid separation procedure to obtain a pure ^{144}Ce by using solvent extraction and pure ^{144}Pr by using extraction chromatography. This procedure is established to be a simple and a practically convenient technique for a demonstration experiment in any educational institution with minimum or no possibility of any spread of contamination.

2. Experimental Details

2.1. Materials and Instruments. All chemicals used in this work were only of analytical grade unless mentioned oth-

erwise. Di-(2-ethylhexyl) phosphoric acid (HDEHP) was obtained from BDH Chemicals, England while Amberlite XAD-7 (20-60 mesh) and Dowex 50W×8 (100-200 mesh) cation exchange resins were obtained from Sigma Aldrich Co., France. Nitric acid and n-hexane were obtained from Loba Chemie, India. The assay of the gamma emitting radionuclides was accomplished by gamma spectrometry using an HPGe detector with 30% efficiency and having resolution of 1.85 keV at 1332 keV of ^{60}Co along with an associated 8k multichannel analyser (MCA) system (Canberra Eurisys; Aptec spectra software). Energy calibration of the HPGe detector was established using ^{241}Am , ^{137}Cs , ^{133}Ba and ^{152}Eu as standard sources (Amersham, Inc.). The detection efficiency was established previously as a function of gamma-ray energy from 244 to 1408 keV using ^{152}Eu standard source before the assay of the samples having same dimensions of the standard in the reproducible geometry. A well-type NaI (TI) detector with a resolution of 8% at 661.6 keV of ^{137}Cs was procured from The Harshaw Chemical Co., (Division of Kewanee Co., USA) was also used to assay the total activity of ^{144}Ce - ^{144}Pr . The stock fuel dissolver solution was obtained by dissolving the Fast Breeder Test Reactor (FBTR)-irradiated mixed oxide ((U, Pu) O_2) pellets in 12 M nitric acid with its associated burn-up of 112 GWd/t. An initial inventory of the stock fuel dissolver solution of the major radionuclides along with their half-lives is shown in Table 3.

2.2. Separation of ^{144}Ce - ^{144}Pr from the fuel dissolver solution by using ion-exchange chromatography.

Measurement of Distribution ratios

In order to standardize the procedure for the purification of ^{144}Ce - ^{144}Pr fraction from other activated and fission products by ion-exchange chromatography, the distribution ratio was measured for the Dowex 50W×8 (100-200 mesh) resin as a function of acidities using simulated solution containing the fission products as that of the dissolver solution described in the previous section. The simulated solution of 5 mL for the long-lived fission products i.e. ^{144}Ce , ^{137}Cs and ^{90}Sr as well as the activated products i.e. ^{60}Co and ^{54}Mn was prepared using their respective tracers in the range of kBq to MBq. Their distribution ratios were determined for Dowex resin over a range of nitric acid concentrations. A known amount (ca. 100 mg) of Dowex 50W×8 (100-200 mesh) resin was taken with the required amount of simulated solution of the tracers in test tubes containing nitric acid of different concentrations i.e. 0.5, 1, 2, 4 and 6 M. The above mentioned tubes were equilibrated for a period of 4 h using a rota-spin. The solution-resin mixture in the tubes was subjected to the centrifugation for a period of 10 min with speed of 10000 rpm and relative centrifugal force of $1700 \times g$, subsequently. The aliquot of the clear solution was sampled out and assayed by gamma spectrometry using HPGe detector.

Separation of ^{144}Ce - ^{144}Pr from Fuel Dissolver Solution

An aliquot of the stock solution of the above referred fuel dissolver solution was taken in a small beaker and was dried under IR lamp. The residue was taken into a 1 mM nitric acid which became the feed for the ion exchange column used in the subsequent separation studies. The Dowex 50W×8 (100-200) resin of 1 g in 1 mM HNO_3 medium soaked over-night was made into a slurry. The same was loaded into a chromatographic glass column of the dimension of 25 cm length and 0.8 cm ID forming a bed height of about 4 cm. The column was initially conditioned using 1 mM nitric acid. The feed solution was introduced into the column and the elution was carried out initially using 80 mL of 1 M nitric acid followed by further elution of about 20 mL of 6 M nitric acid. A flow rate of 0.4-0.5 mL/min was maintained throughout this experiment. The samples of the uniform size of 10 mL were collected during

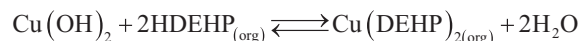
TABLE 3: Activities of fission and activation products present in the stock fuel dissolver solution

| No. | Fission / Activation Product | Half-life (y) | Activity (kBq) |
|-----|---------------------------------------|---------------|----------------|
| 1 | ^{106}Ru - ^{106}Rh | 1.02 | 780 |
| 2 | ^{125}Sb | 2.76 | 400 |
| 3 | ^{134}Cs | 2.06 | 280 |
| 4 | ^{137}Cs | 30.1 | 11300 |
| 5 | ^{144}Ce - ^{144}Pr | 0.78 | 4300 |
| 6 | ^{154}Eu | 8.59 | 66 |
| 7 | ^{54}Mn | 0.86 | 14 |
| 8 | ^{60}Co | 5.27 | 3.7 |

the elution and the same were assayed using HPGe detector.

2.3. Purification of ^{144}Ce from its in-grown-daughter-in-equilibrium ^{144}Pr by using Solvent Extraction.

The extractant HDEHP was used in the present study to purify the ^{144}Ce fraction obtained from the above separation from its in-grown daughter-in-equilibrium ^{144}Pr as well as from the other minor impurity of ^{154}Eu . While the pure HDEHP is a clear colourless solvent, it is amber in case of commercial HDEHP. The purification of the commercial HDEHP was accomplished through the selective precipitation of its copper complex [23]. Approximately 1M HDEHP in cyclohexane was saturated with copper (II), by equilibrating the above organic phase with an aqueous solution of CuSO_4 mixed with NaOH . Acetone was added, on stirring, to the organic phase separated from the above mixture which resulted into the precipitation of Cu-HDEHP complex.



The $\text{Cu}(\text{DEHP})_2$ precipitate was filtered subsequently; washed with acetone, air dried and converted back to pure HDEHP by contacting it with 0.5 M hydrochloric acid and millipore water. The acid washings with HCl were repeated to remove all the copper from the HDEHP phase. The clear HDEHP phase was contacted with millipore water three to four times to remove the dissolved acid. Further, the water was evaporated off from the purified fraction of HDEHP using a rotary evaporator at about 60 °C. The purified HDEHP was used for the subsequent separation studies.

The ^{144}Ce - ^{144}Pr sample fraction with the trace impurities of ^{154}Eu obtained as described above was evaporated to the dryness under IR lamp. The dried residue was taken into 5 mL of concentrated HNO_3 to which a 30 mL of 1 M potassium bromate in 9 M HNO_3 was added. From this stock solution, a 10 mL fraction was taken into a separating funnel along with freshly prepared 1 M KBrO_3 in 9 M HNO_3 and 0.7 M HDEHP in n-heptane of 5 mL each. The mixture was equilibrated manually for about 5 minutes and allowed to stand for about a minute for its phase separation. The samples of the organic phase of about 2 and 5 mL were sampled out for an immediate assay of the total activity using NaI (TI) as well as HPGe detectors, respectively for the assay of parent ^{144}Ce and the in-grown daughter ^{144}Pr .

2.4. Demonstration of Secular Equilibrium behaviour of

^{144}Ce - ^{144}Pr . The sample assay was carried out using a well-type NaI (TI) scintillation detector in an integral mode. The total activity of the sample was recorded by counting it in regular intervals for a period of about two hours. The initial countings were noted for a counting period of 30 s with a gap of the same duration between the successive countings for a

period of first 20 min beyond which the gap was increased from 1 to 5 min maintaining the same counting period of 30 s for the duration of next 100 min again. Further, the 5 mL sample was also assayed simultaneously using HPGe detector to monitor the growth of the daughter ^{144}Pr for the comparison and confirmation. The decay curve was plotted for the total activity data obtained from NaI (TI) detector as a function of time on a semi-log graph paper.

2.5. Purification of the daughter nuclide ^{144}Pr by using extraction Chromatography. A measured quantity of Amberlite XAD-7 beads were washed with 4 M HNO_3 , distilled water and acetone successively after which the same was dried at 40 °C in vacuum [24]. The purified XAD-7 resin was weighed accurately and taken with the appropriate amount of HDEHP corresponding to 40% (w/w) HDEHP/XAD7 resins in a reagent bottle containing the diluent n-hexane. This mixture was equilibrated for 2 h in a mechanical shaker. After the equilibration, the diluent, n-hexane was evaporated using a rota-evaporator and the resin was further dried at 60 °C for about an hour. Mass balance for the coated resin with respect to the initial weight (XAD7+HDEHP) was observed to be around 95% - 100%.

About 5 g of the above HDEHP coated XAD-7 resin in n-hexane in its slurry form was loaded into a glass column with the dimension of 25 cm length and 1 cm ID that resulted into a resin bed height of 10 cm. The column was conditioned using 1 M KBrO_3 in 9 M HNO_3 medium. The mixture solution containing ^{144}Ce - ^{144}Pr in 1 M KBrO_3 - 9 M HNO_3 medium was loaded in to the column. The immediate elution was initiated using 1 M KBrO_3 in 9 M HNO_3 at a flow-rate of 0.8-0.9 mL/min. Sample fractions of 15 mL were collected and assayed for its activity using HPGe detector. At the end of the elution, the chromatographic column was washed with 9 M HNO_3 in order to maintain the column completely free from the eluant KBrO_3 .

3. Results and Discussion

3.1. Separation of ^{144}Ce - ^{144}Pr from the fuel dissolver solution by using ion-exchange chromatography.

Measurement of Distribution ratios

All the equilibrated samples from batch studies were assayed by HPGe detector and the distribution ratios (D_M) were calculated using the following equation.

$$D_M = \frac{(A_0 - A)V}{M}$$

where A_0 and A are the activities (cps) of the elements in the aqueous phase before and after equilibration with the resin, respectively; V is the volume of the solution kept for equilibration (mL) and M is weight of the resin (g). The distribution ratios for the different radio tracers, representing various fission and activated products present in the dissolver solution were determined as function of nitric acid concentration for the Dowex resin. The data obtained are plotted as shown in Fig. 2. It is observed from the graph that the D_M values of all the tracers decreased exponentially with the increased concentration of nitric acid in the range of study. The decrease in D_M values of metal ions at increased nitric acid concentration is owing to the higher competition of H^+ ions towards the functional sites of resin. It was also observed that the D_M values of Ce were always higher than that of the other tracers over a range of nitric acid concentration i.e. up to 4 M nitric acid which is due to its higher ionic potential.

This observation may be attributed to the relatively stronger interaction of Ce with cation exchange resin in comparison with the other fission products in the simulated solution owing to its relatively higher ionic potential i.e. charge to radius ratio.

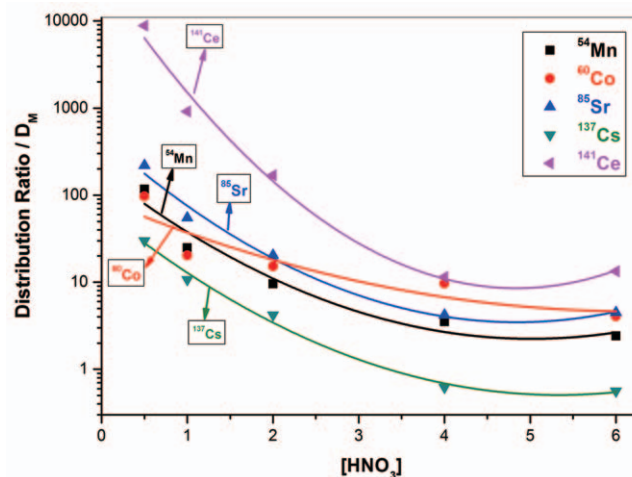


Figure 2. Variation of the distribution ratios with the nitric acid concentration in the DOWEX 50W×8 (100–200 mesh) resin. (Amount of resin in each tube: 50 mg; Volume of the HNO_3 solution: 5 mL; Equilibration time: 4 h; Assay: Gamma Spectrometry using HPGe detector).

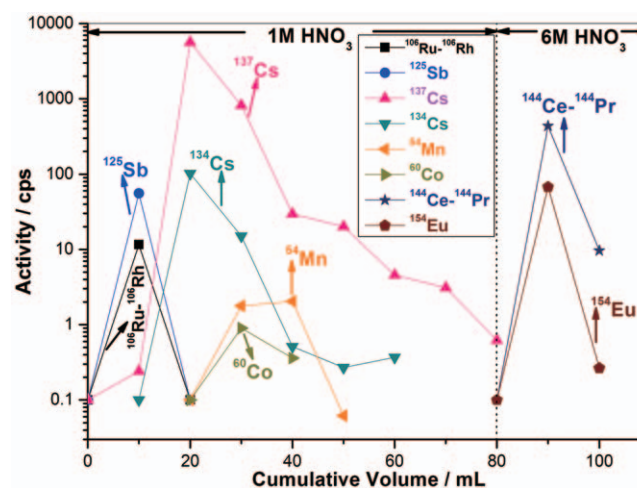


Figure 3. Elution profile for the separation of ^{144}Ce from fission and activation products using cation exchange chromatography. (Amount of Dowex resin: 1 g; Column Dimensions: 0.8 cm ID, 25 cm length and 4 cm bed height; Conditioning: 1 mM Nitric acid; Feed: Fission product solution in 1 mM HNO_3 ; Flow rate: 0.4-0.5 mL/min; Assay: Gamma Spectrometry using HPGe detector).

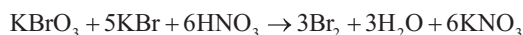
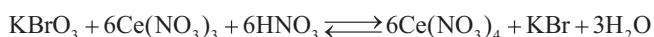
Even though, the distribution ratio and the separation factor were observed to be higher and comparable for Ce at both 0.5 M as well as 1 M HNO_3 , the latter concentration was chosen as the same yielded a baseline separation of Ce from other fission products by ion-exchange chromatography, in a relatively less volume of eluant.

Separation of ^{144}Ce - ^{144}Pr from Fuel Dissolver Solution

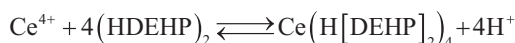
The separation profile for the fission products using Dowex resin column was established and the elution profile is shown in Fig. 3. It is observed that the fission products such as ^{137}Cs , ^{134}Cs , ^{125}Sb , ^{106}Ru - ^{106}Rh and more importantly the activation products ^{54}Mn and ^{60}Co were all eluted in the initial fractions with 1 M nitric acid as the eluting agent. This is due to the lower distribution ratio values of these metal ions at the eluant concentration of 1 M HNO_3 . Cerium was eluted last owing to its very high distribution ratio and collected in a small fraction using 6 M HNO_3 along the other lanthanides i.e. in-grown ^{144}Pr and traces of ^{154}Eu impurity. Thus, a lanthanide group separation from other fission products is performed initially followed by a specific isolation of cerium from the lanthanide group to

be carried out to demonstrate the secular equilibrium behaviour subsequently.

3.2. Purification of ^{144}Ce from its in-grown-daughter-in-equilibrium ^{144}Pr by Solvent Extraction. The secular equilibrium phenomenon was demonstrated conveniently using the pure fraction of ^{144}Ce including its purification from its in-grown daughter product ^{144}Pr . The variation in the total counts of the pure ^{144}Ce fraction was profiled using NaI (TI) detector that included the associated growth of the daughter product ^{144}Pr there on. Purification of ^{144}Ce from its in-grown daughter product, ^{144}Pr is a challenging task owing to the fact that they both belong to the same lanthanide series and their separation is made difficult by the nature of their inherent complicated separation chemistry owing to the similar oxidation state of +3 as well as their similar chemical behaviour due to the phenomenon of lanthanide contraction. However, Cerium also has another stable oxidation state of +4 [15, 24] which facilitates its separation both from the other lanthanides as well as the fission products. Initially, the lanthanides i.e. ^{144}Ce - ^{144}Pr and ^{154}Eu were separated from the other fission products by ion-exchange chromatography followed by the individual separation of ^{144}Ce (IV) from the lanthanide fraction using solvent extraction technique. Separated fraction of pure ^{144}Ce (IV) gets quickly contaminated with its in-grown daughter nuclide ^{144}Pr and hence requires fresh purification every time to obtain a pure fraction of the parent nuclide ^{144}Ce . The purification of the parent fraction from its daughter ^{144}Pr is carried out by adding 1 M KBrO_3 solution that converts all the Ce (III) into a single and uniform oxidation state of Ce (IV) and facilitates its efficient extraction by the extractant HDEHP from the other lanthanides as well [24-25], which is shown below.



^{144}Ce was extracted into the organic phase (HDEHP) while the daughter product ^{144}Pr was retained in aqueous phase. HDEHP exists as a dimer in dilute organic medium as $(\text{HDEHP})_2$. The nature of the extracted species depends on the nature of the acid in the aqueous phase and its concentration [26]. The extraction of cerium (IV) from nitric acid medium to the organic phase is represented as follows [27-29].



The purified ^{144}Ce in the organic phase was assayed by using a NaI (TI) detector to demonstrate the secular equilibrium phenomenon.

3.3. Demonstration of Secular Equilibrium behaviour of ^{144}Ce - ^{144}Pr . The time interval between the end of separation of pure ^{144}Ce and to the beginning of assay in the experiment must be as short as possible to precisely profile the variation of the total activity as well as the growth of the daughter ^{144}Pr . The pure parent sample was counted by well type NaI (TI) scintillation detector and the total activity there on was monitored periodically for a period of about two hours. The initial delay of seven minutes to assay the purified fraction was due to the practical delay in bringing the sample to the detector after its separation. The total activity was observed to increase initially which remained apparently constant after some time. The initial increase in the total activity was due to the in-growth of the daughter nuclide ^{144}Pr from its pure parent ^{144}Ce . The total activity remained apparently constant due to the subsequent achievement of radioactive equilibrium.

The total activity of ^{144}Ce - ^{144}Pr pair from the NaI (TI) detector was plotted as a function of time (curve a) using a semi-log

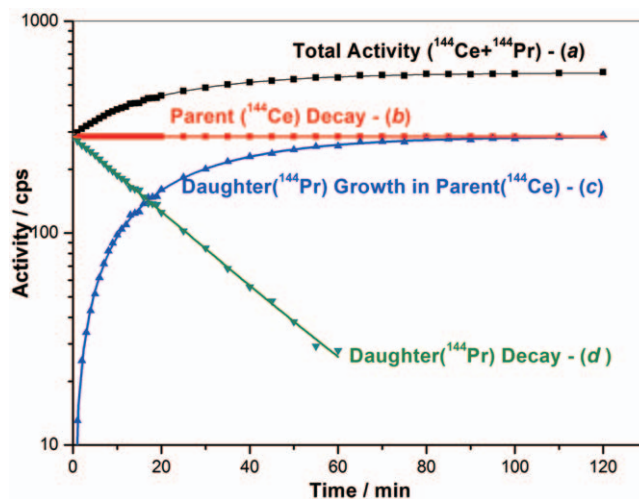


Figure 4. Demonstration for secular equilibrium using ^{144}Ce - ^{144}Pr pair. (Sample details: 2 mL of pure ^{144}Ce fraction separated by solvent extraction using HDEHP & the total activity assay by using NaI (TI) scintillation detector).

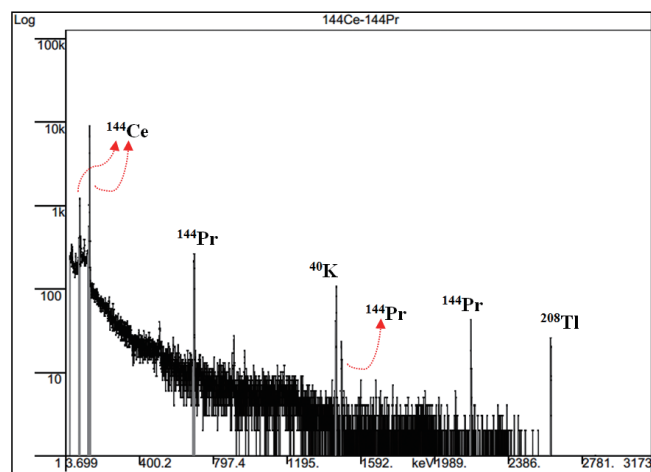


Figure 5. Gamma spectrum of ^{144}Ce - ^{144}Pr secular equilibrium pair by HPGe detector. (Sample details: 5 mL of pure ^{144}Ce fraction separated by solvent extraction using HDEHP and assay by using HPGe detector).

graphical pattern as shown in Fig. 4. As there was some short time delay between the separation of pure ^{144}Ce and its initial counting, the missing data points during this period were obtained by back-extrapolating the total activity data to the Y-axis. By using this plot, individual profiles i.e. profiles of the parent decay, daughter growth in parent and daughter decay were resolved (Fig. 4).

'Parent decay' profile (curve b) was obtained by drawing a straight line parallel to the linear portion of the total activity from the point of total activity at zero time. 'Daughter growth in parent' (curve c) line was obtained by subtracting parent activity curve from the 'Total activity' (curve a). 'Daughter decay' (curve d) was profiled by subtracting daughter growth in parent curve (curve c) from parent activity curve (curve b). This corresponds to the independent decay profile of daughter activity, separated from the parent in-equilibrium. The half-life of the daughter ^{144}Pr was determined using its decay curve which was found to be 17.14 ± 0.17 min and agreed well with the reported value of 17.29 min [13, 14].

The ^{144}Ce - ^{144}Pr pair which is in secular equilibrium was analysed by high resolution gamma spectrometry using HPGe detector. The gamma spectrum of the same sample is shown in Fig. 5. The spectrum indicated the presence of parent ^{144}Ce which was extracted in its pure form into organic phase and

the in-grown daughter ^{144}Pr from the same. The long lived ^{144}Ce parent shows no significant change in decay rate except the variation due to the statistics during the period of experiment, while the daughter ^{144}Pr grows in to a constant value. The rate at which the daughter ^{144}Pr grows to this constant value depends on its half-life and not on that of parent ^{144}Ce . This experiment demonstrates the parent-daughter relationship in the phenomenon of secular equilibrium satisfactorily.

3.4. Determination of half-life using the pure fraction of ^{144}Pr obtained by extraction chromatography. The extraction chromatographic studies were carried using 40% (w/w) HDEHP-XAD7 resin. The column was conditioned with KBrO_3 to maintain the Ce oxidation state in +4, so that it binds strongly to the resin. The gamma spectrometric analysis of the eluted fractions in the medium of 1 M KBrO_3 in 9 M HNO_3 showed the presence of ^{144}Pr only, indicating that all the ^{144}Ce was held strongly with the resin. The purified ^{144}Pr fraction was assayed continuously by HPGe detector to obtain its corresponding decay curve.

The pure ^{144}Pr fraction was assayed regularly by high resolution gamma ray spectrometry using HPGe detector for 75 min and obtained its corresponding decay profile (Fig. 6). The half-life obtained from the decay profile was found to be 17.32 ± 0.64 min and was in good agreement with the reported value i.e. 17.29 min [13, 14]. The half-life value of the daughter nuclide ^{144}Pr obtained from the pure fraction yielded a more accurate value compared to the value (17.14 min) obtained by secular equilibrium graph as discussed earlier, indicating the purity of the daughter nuclide.

4. Conclusion

^{144}Ce - ^{144}Pr pair was purified from fission products and activation products in the FBTR irradiated (U, Pu) O_2 fuel dissolver solution in nitric acid medium using ion-exchange chromatography. The separation of pure parent (^{144}Ce) from the ^{144}Ce - ^{144}Pr pair was accomplished by solvent extraction method using 0.7 M HDEHP/n-heptane as the extractant. The pure ^{144}Ce fraction was assayed continuously for a particular duration using well type NaI (Tl) solid scintillation detector. The total activity due to both parent ^{144}Ce and its in-grown daughter ^{144}Pr was profiled as a function of time using a semi-log paper. The curve was resolved into its individual components such as parent decay, daughter growth in its parent and independent decay of daughter. The daughter nuclide ^{144}Pr was purified from its parent in-equilibrium ^{144}Ce by extraction chromatographic technique using HDEHP impregnated XAD7 resin with KBrO_3 - HNO_3 as the eluant. Half-life of ^{144}Pr was obtained from this graph and found to be 17.32 ± 0.64 min which is in agreement with the value obtained from secular equilibrium graph i.e. 17.14 ± 0.17 min. Thus the half-life values obtained from pure fraction ^{144}Pr as well as equilibrium curve were in agreement with the reported value, namely, 17.29 min. Thus the phenomenon of secular equilibrium was demonstrated using the pure fraction of ^{144}Ce satisfactorily.

References

- (1) G. Friedlander, J. W. Kennedy, E. S. Macias and J. M. Miller, Nuclear and Radiochemistry, 3rd ed. (John Wiley and Sons, Inc., New York, 1981).
- (2) H. J. Arnikar, Essentials of nuclear chemistry, 4th ed., (New Age International (P) Ltd. Publishers, New Delhi, 2007).
- (3) G. R. Gilmore, Practical Gamma-ray Spectrometry, 2nd ed. (John Wiley and Sons, Inc., England, 2008).
- (4) J. R. Prince, J. Nucl. Med. 20, 162 (1979).
- (5) G. R. Choppin and C. L. Nealy, J. Chem. Educ. 41, 598

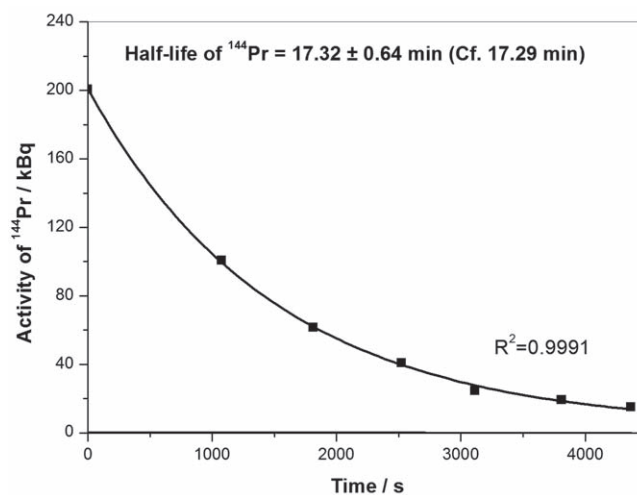


Figure 6. Decay profile of ^{144}Pr . (Amount of resin: 5 g of 40% w/w HDEHP coated XAD7; Column Dimensions: 10 mm ID, 25 cm length and 10 cm bed height; Conditioning: 1 M KBrO_3 in 9 M HNO_3 ; Feed: tracer mixture (^{144}Ce - ^{144}Pr) in 1 M KBrO_3 /9 M HNO_3 ; Flow rate: 0.8-0.9 mL/min; sample volume: 15 mL; Assay: Gamma Spectrometry using HPGe detector).

- (1964).
- (6) H. Arino and H. H. Kramer, Int. J. Appl. Radiat. Isot. 24, 197 (1973).
- (7) J. S. Walter, H. Arino, and K. H. Herman, Int. J. Appl. Radiat. Isot. 29, 575 (1978).
- (8) W. F. Semmelrogge, and F. Sicilio, J. Chem. Educ. 42, 427 (1965).
- (9) M. F. L'Annunziata, J. Chem. Educ. 48, 700 (1971).
- (10) V. P. Chechev, and M. M. Bé, Appl. Radiat. Isot. 87, 132 (2014).
- (11) D. V. Filosofov, M. Garland, K. D. John, F. F. Knapp, R. Kuznetsov, L. Mausner, S. Mirzadeh, M. R. A. Pillai, B. Ponsard, F. Roesch, R. J. Ruth and S. K. Samanta, IAEA Radioisotopes and Radiopharmaceuticals Series No. 2, IAEA, Vienna, 2010, pp. 1-111.
- (12) E. A. C. Crouch, At. Data Nucl. Data Tables. 19, 417 (1977).
- (13) B. V. N. Rao, and G. N. Rao, J. Phys. Soc. Jpn. 40, 1 (1976).
- (14) S. Raman, Nucl. Phys. A 107, 402 (1968).
- (15) T. Bjørnstad, J. I. Borroto Portela, P. Brisset, N. Chankow, J. S. Charlton, M. A. Conejo Solis, C. P. K. Dagadu, A. Dash, F. Diaz Vargas, Ghiyas-Ud-Din, J. H. Jin, Li Jinfu, L. Muñoz Anrique, A. Pinto Ferreira, J. M. Palige, F. Roesch, J. Sung-Hee and C. Vargas, Radiotracer Generators for Industrial Applications, IAEA Radiation Technology Series No. 5, IAEA, Vienna, (2013) p. 124.
- (16) J. T. Douglas, M. J. Goss, D. Hill, Soil and Tillage Research, 1, 11 (1980).
- (17) A. V. Harms, S. M. Jerome, J. Radioanal. Nucl. Chem. 264, 517 (2005).
- (18) Valéry Olivier Zilio, Om Parkash Joneja, Yuri Popowski, François Oswald Bochud, Rakesh Chawla, Int. J. Radiation Oncology Biol. Phys. 62, 585 (2005).
- (19) C. Cappellini, A. Airoidi, M. Alemi, M. Amati, C. Bianchi, A. Bulgheroni, M. Caccia, L. Conte, W. Kuciewicz, M. Prest, E. Vallazza, C. Sampietro, Nucl. Instr. Meth. Phys. Res. A 527, 46 (2004).
- (20) E. R. Tompkins, S. W. Mayer, J. Am. Chem. Soc. 69, 2859 (1947).
- (21) D. Mac Donald, Anal. Chem. 33, 1807 (1961).
- (22) A. Bradley and M. Adamowicz, J. Chem. Educ. 36, 136 (1959).
- (23) J. A. Partridge and R. C. Jensen, J. Inorg. Nucl. Chem. 31,

- 2587 (1969).
- (24) R. Kumar, N. Sivaraman, A. Thiruvankadasamy, C. R. Venkata Subramani, and P. R. Vasudeva Rao, *J. Radioanal. Nucl. Chem.* 251, 21 (2002).
- (25) A. R. Landgrebe, R. H. Rodriguez - Pasques and F. J. Schima, *Int. J. Appl. Radiat. Isot.* 19, 147 (1968).
- (26) V. K. Manchanda, P. N. Pathak and P. K. Mohapatra, *New Developments in Thorium, Uranium, and Plutonium Extraction*, Bruce A Moyer (Eds.), Ion Exchange and Solvent Extraction, A Series of Advances, CRC Press, 19, pp. 65–118 (2009) DOI: 10.1201/9781420059700-c2.
- (27) R. Lundqvist, L.U. JIU-FANG and I. Svantesson, *Acta. Chem. Scand. A* 37, 743 (1983).
- (28) T. S. Grimes, P. R. Zalupski and L. R. Martin, *J. Phys. Chem. B* 118, 12725 (2014).
- (29) P. H. Tedesco, V. B. De Rumi and J. A. G. Quintana, *J. Inorg. Nucl. Chem.* 29, 2813 (1967).