

Separation of no-carrier-added ^{149}Gd from ^{12}C activated natural praseodymium matrix

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Abstract ^{149}Gd was produced from the ^{12}C induced reaction on natural praseodymium target. No-carrier-added (nca) ^{149}Gd was separated from the bulk target matrix by liquid–liquid extraction (LLX) using cation exchanger di-(2-ethylhexyl)phosphoric acid (HDEHP) dissolved in cyclohexane. High separation factor of 2,450 was achieved at the optimal experimental condition when 1% HDEHP and 0.1 M HCl were used as organic and aqueous phases respectively. The result was also compared with the previous reports.

Keywords No-carrier-added ^{149}Gd · ^{12}C induced reaction · Natural praseodymium target · Heavy ion activation · Liquid–liquid extraction · Radiochemical separation

Introduction

The applications of lanthanide radionuclides are limited compared to that of other elements in the Periodic Table. One of the reasons of this fact may be due to the non-availability of suitable radionuclides of lanthanide elements in the no-carrier-added (nca) form. Neutron activation leads to radionuclides of low specific activity. Light ions, like α or p, activation on lanthanide elements leads to nca radionuclides but the separation becomes a colossal task due to the similar

physicochemical properties of the adjacent lanthanides, especially when the nca radionuclide is in ultra-trace amount and bulk target is of milligram quantity. To get rid of this painstaking problem in separating nca radiolanthanides, for the first time, Lahiri et al. [1] proposed heavy ion activation, which essentially introduced large difference in atomic number between the product and the target elements, and in turn the separation of nca radiolanthanide from the bulk target became easier. Since then a large number of publications came out on the heavy ion assisted production of nca radionuclides including the radiolanthanides from the same group in a continuous endeavor.

^{153}Gd radionuclide has found applications in the diagnostic nuclear medicine including scanning of lumbar vertebrae and femoral neck. The ^{153}Gd –DTPA tracers act as potential MRI contrast agent. ^{153}Gd is a candidate radionuclide for the detection of brain tumour and in scanning bone marrow without any toxicity. The uptake of Gd–DTPA in acute myocardial infarction may be a marker of acute myocardial necrosis [2, 3]. However, ^{153}Gd has long half-life of 241.6 days, which is certainly a disadvantage for clinical applications. In this circumstance, comparatively short-lived ^{149}Gd (9.4 days), having intense γ -rays, may act as a potential alternative of ^{153}Gd . Production of nca ^{149}Gd and its purification from the target matrix is therefore important for in vivo applications. The present report aims for the high purity nca ^{149}Gd from natural praseodymium target by ^{12}C activation.

The literature on the separation of Gd from other lanthanides, either as nca product or in trace scale is not too rich. There are very few reports on such separations [4]. Earlier the extraction and extraction chromatographic behaviors of ^{153}Gd along with Sm, Eu and Tb in the di-(2-ethylhexyl)phosphoric acid (HDEHP)–decane– HNO_3 system were studied by Melnik et al. [5]. They obtained

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purification factor for gadolinium of about 100 with respect to Sm and Tb impurities and about 2 with respect to Eu impurity. Nayak and Lahiri [6] studied liquid–liquid extraction (LLX) of trace level cerium and gadolinium (^{141}Ce and ^{153}Gd) from HCl and HNO_3 media with liquid cation exchanger, HDEHP. A quantitative separation of the elements from an admixture of the two radioisotopes was achieved with 0.1% HDEHP and 0.01 M HCl solution. Later on authors separated nca gadolinium isotopes $^{147,149}\text{Gd}$ from 80 MeV ^{12}C activated $^{\text{nat}}\text{CeO}_2$ target. They achieved separation of nca Gd (with 55% yield) by 1% HDEHP dissolved in cyclohexane from 10^{-4} M HCl solution [7]. Earlier, the same group had demonstrated the production of $^{147,149}\text{Gd}$ and ^{147}Eu in 70 MeV ^{11}B irradiated praseodymium foil target [8]. The nca gadolinium and europium radionuclides were separated from bulk target by LLX using HDEHP. In this paper, we describe an alternative approach for the production of nca Gd by irradiating praseodymium foil with ^{12}C beam and compared the results with our earlier reports.

Experimental

Production of nca Gd

A natural praseodymium (^{141}Pr) foil of 99.9% purity, procured from Alfa Aesar, was used to prepare a self supporting metal target of 15 mg/cm^2 thickness by proper rolling. The $^{\text{nat}}\text{Pr}$ target was irradiated by 71.5 MeV $^{12}\text{C}^{6+}$ ions at the BARC-TIFR Pelletron facility, Mumbai, India, for 560 min. At the end of bombardment (EOB), a total charge of $1,428\ \mu\text{C}$ was measured by an electron suppressed Faraday cup placed at the rear of the target. An aluminum catcher foil of 3 mg/cm^2 was used to stop the recoiled evaporation residues, if any, in the beam direction.

In order to monitor the fate of the bulk praseodymium in the radiochemical separation, it is important to produce praseodymium radionuclides, which are hardly produced in the $^{12}\text{C} + ^{\text{nat}}\text{Pr}$ reaction. Therefore, a separate $^{\text{nat}}\text{Pr}$ foil was irradiated in the neutron flux of $5.0 \times 10^{12}\text{ n cm}^{-2}\text{ s}^{-1}$ for 4 h in the CIRUS reactor, BARC, Mumbai, India, to produce ^{142}Pr (19.12 h).

At the EOB, target foils were assayed by off line γ -spectrometry using an n-type HPGe detector (CANBERRA) coupled with a PC based multi-channel analyzer, PCA2 (OXFORD), to obtain the activity of the product radionuclides. The detector had energy resolution of 2.13 keV at 1,332 keV. Efficiency calibration of the detector was performed using standard sources, ^{152}Eu (13.506 years), ^{133}Ba (10.54 years) and ^{137}Cs (30.0 years) of known activity. Nuclear spectroscopic data of the radionuclides discussed in this report are tabulated in Table 1 [9].

The γ -spectrometric analysis of irradiated target assured the production of nca ^{149}Tb and ^{149}Gd radionuclides in the target matrix. ^{149}Gd was produced via $^{141}\text{Pr}(^{12}\text{C},\text{p}3\text{n})^{149}\text{Gd}$ and $^{141}\text{Pr}(^{12}\text{C},4\text{n})^{149}\text{Tb}(\text{EC})^{149}\text{Gd}$ reactions. After the complete decay of short-lived ^{149}Tb (4.118 h), nca ^{149}Gd was separated from the bulk praseodymium target.

Radiochemical separation

The ^{12}C irradiated $^{\text{nat}}\text{Pr}$ foil and neutron irradiated $^{\text{nat}}\text{Pr}$ foil, were separately dissolved in the minimum volume of 0.1 M HCl. The ^{12}C irradiated target solution was spiked with ^{142}Pr tracer solution and evaporated to dryness in order to attain the same chemical form between radioactive ^{142}Pr tracer and bulk Pr. The residue was then re-dissolved into 0.01 M HCl to prepare active uniform mixture of nca product and target matrix.

Separation of nca Gd from bulk praseodymium was approached by LLX. Series of LLX experiments were

Table 1 Nuclear reactions, Q values and nuclear spectroscopic data [9] of the product radionuclides

Nuclear reaction	Product	Q value (MeV)	E_{th} (MeV) (calculated)	$T_{1/2}$	E_{γ} (keV)	I_{γ} (%)
$^{141}\text{Pr}(^{12}\text{C},4\text{n})$	^{149}Tb	−46.810	50.796	4.118 h	164.98	26.4
					352.24	29.4
					496.24	14.6
$^{141}\text{Pr}(^{12}\text{C},3\text{n})$	^{150}Tb	−39.12	42.46	3.48 h	638.05	72
					251.863	26.3
$^{141}\text{Pr}(^{12}\text{C},2\text{n})$	^{151}Tb	−30.53	33.13	17.609 h	108.088	24.3
					287.357	28.3
$^{141}\text{Pr}(^{12}\text{C},\text{p}3\text{n})$	^{149}Gd	−42.39	46.00	9.28 days	149.735	48
					298.634	28.6
$^{141}\text{Pr}(^{12}\text{C},4\text{n})^{149}\text{Tb}(\text{EC}/\beta^+)$	^{149}Gd					
$^{141}\text{Pr}(\text{n},\gamma)$	^{142}Pr	5.843		19.12 h	1575.6	3.7

carried out using the cation extracting agent HDEHP (1% v/v) dissolved in cyclohexane as organic phase and dilute HCl as aqueous phase. In each extraction, 3 mL of organic solution was shaken for 10 min in a mechanical shaker with equal volume of aqueous HCl and 100 μL of activity. Then liquid mixture was left for the complete phase separation. In order to determine the distribution of activities, 2 mL of aliquot was collected from each phase for γ -spectrometric study. In an extraction series, concentration of HCl was varied from 10^{-5} to 1 M keeping the HDEHP concentration fixed to 1% (v/v) and in the next series, the concentration of HDEHP was varied with respect to fixed 0.1 M HCl. In the third set of extraction, concentration of HDEHP was varied at a fixed 0.1 M HCl in presence of

H_2O_2 . Nca Gd radionuclides were back extracted to the aqueous phase from HDEHP using both 6 M HCl and 0.1 M DTPA in 1 M NaOH separately. All the chemicals used for the chemical separation were of analytical grade.

Results and discussion

The ^{12}C activated natural praseodymium target was assayed at different time intervals by γ -spectrometry. Analysis of the γ -spectra confirms the production of ^{149}Tb , ^{150}Tb , ^{151}Tb and ^{149}Gd in the Pr target matrix. The batch yield for ^{149}Tb , ^{150}Tb , ^{151}Tb and ^{149}Gd were found to be 86, 37, 7 and 70 kBq/ $\mu\text{A h}$ at EOB, respectively. The amount of nca ^{149}Gd produced in the target matrix is comparable to that of nca ^{149}Tb at EOB. Probably, the production route of nca Gd not only includes its decay through $^{141}\text{Pr}(^{12}\text{C},4n)^{149}\text{Tb}(\text{EC}/\beta^+)^{149}\text{Gd}$ but also includes the possibility of direct production through $^{141}\text{Pr}(^{12}\text{C},p3n)^{149}\text{Gd}$ reaction. However, theoretical calculation using Monte Carlo statistical simulation code, PACE II [10] shows very low cross section for the direct production of ^{149}Gd (Fig. 1). ^{149}Tb has two decay modes, EC (83.3%) and α (17.7%). The irradiation time in the present experiment was long (9.3 h), which is more than two half-lives of ^{149}Tb (4.118 h), and consequently increased the amount of nca ^{149}Gd (9.28 days) at EOB via electron capture. Another important observation is that ^{149}Tb is the low spin (1/2+) state, and the high initial angular

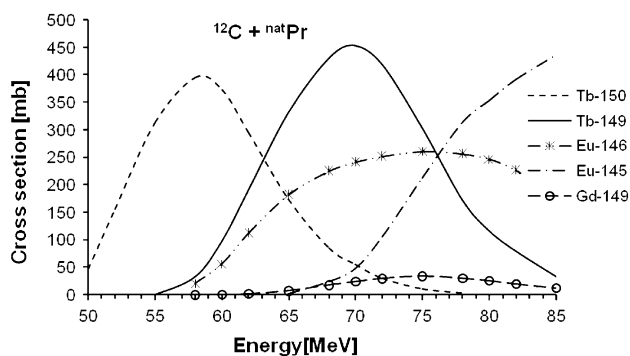
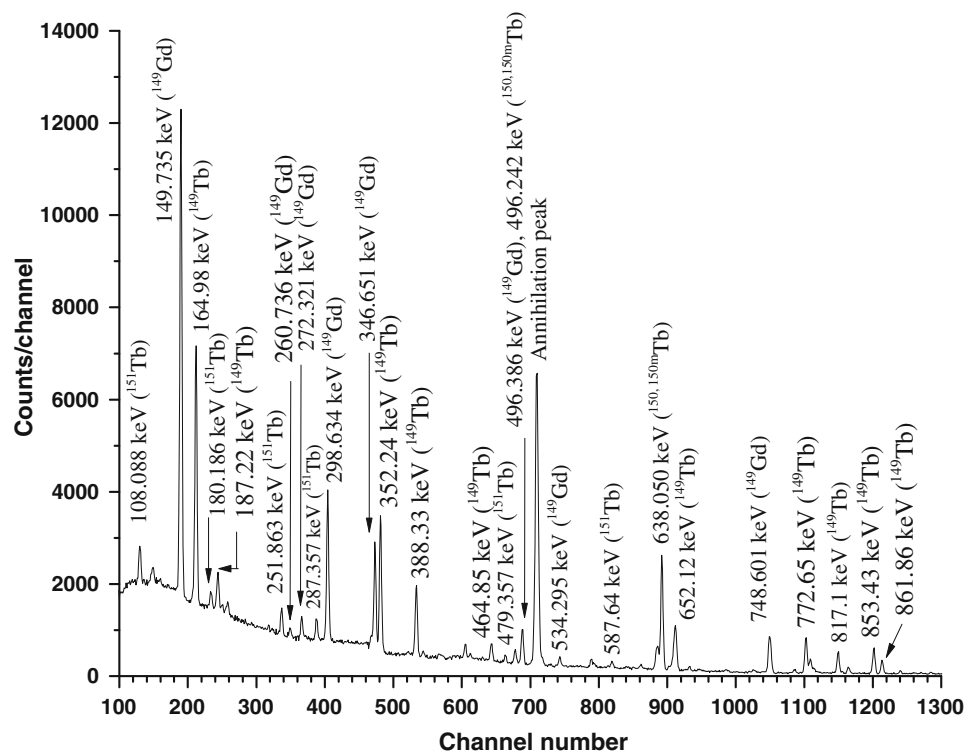


Fig. 1 Theoretical excitation functions of $^{12}\text{C} + \text{natPr}$ reaction as predicted by PACE-II

Fig. 2 Nondestructive γ -spectrum of the ^{12}C activated natural Pr foil after 1.2 h of EOB



momentum involved in the reaction of 71.5 MeV $^{12}\text{C} + ^{141}\text{Pr}$ will result in preferential population of the high spin (11/2 $-$) isomer ($^{149\text{m}}\text{Tb}$). The EC decay of this isomer to ^{149}Gd is responsible for the high yield of the latter as observed in the present experiment. The γ -spectrum of the ^{12}C activated natural praseodymium foil collected after 1.2 h of EOB is presented in Fig. 2. It is interesting to note that contrary to the PACE-II prediction, no evidence of the production of $^{145,146}\text{Eu}$ was observed in the present work.

The radiochemical separations were started 2 days after the EOB ensuring complete decay of ^{149}Tb . Figure 3 represents the extraction behavior of nca Gd and bulk Pr as a function of concentration of HCl at a fixed 1% (v/v) HDEHP dissolved in cyclohexane. At the low concentration of HCl, from 10^{-5} to 10^{-2} M region, nca Gd was extracted to the HDEHP phase along with bulk Pr. The high extractability of lanthanides may be attributed to the formation of cationic aquo-complex like, $[\text{Ln}(\text{H}_2\text{O})_x]^{3+}$ [11] at the lower acidity and extracted to the liquid cation

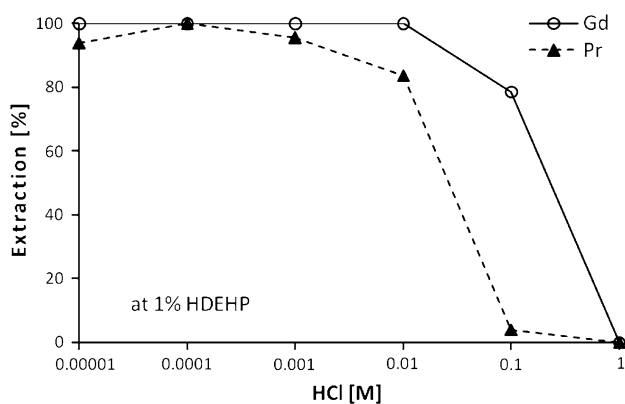


Fig. 3 Extraction profile of nca Gd and bulk Pr in LLX as a function of HCl concentration at a fixed strength of HDEHP (1%)

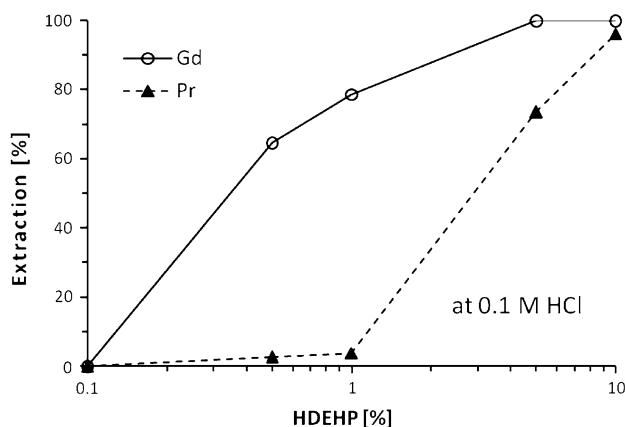


Fig. 4 Extraction profile of nca Gd and bulk Pr in LLX as a function of HDEHP concentration at a fixed strength of HCl (0.1 M)

exchanger HDEHP. A sharp change in the extraction behavior was observed at 0.1 M HCl, where nca Gd was extracted $\sim 79\%$ to the organic phase leaving the bulk praseodymium in the aqueous phase. After 0.1 M HCl concentration, the extractions of both bulk Pr and nca Gd sharply decreased. At 0.1 M HCl and 1% HDEHP concentration, about 4% bulk Pr was extracted to the organic phase with the nca products. In order to improve the separation efficiency, a second series of extraction was carried out by varying the concentration of HDEHP with fixed 0.1 M HCl. The highest separation factor was observed as before, i.e. with 1% HDEHP and 0.1 M HCl (Fig. 4). The extent of separation was further dramatically improved with addition of H_2O_2 to the aqueous phase (Fig. 5). The maximum separation was achieved at 1% HDEHP and 0.1 M HCl in presence of H_2O_2 , where about 80% nca ^{149}Gd was extracted to the organic phase leaving the bulk praseodymium quantitatively in the aqueous phase. A high separation factor ($D_{\text{Gd/Pr}}$) of 2.45×10^3 was achieved in this optimum condition. The addition of H_2O_2 increased the separation factor probably due to the fact that H_2O_2 helped Pr to obtain Pr^{4+} , which eventually increased the difference of ionic radii between Pr^{4+} and Gd^{3+} and as a consequence the difference between the extraction behaviors of these two elements increased. Nca ^{149}Gd was back extracted from the organic phase using 6 M HCl and 0.1 M DTPA in 1 M NaOH. The distribution coefficients and separation factors at the optimal conditions have been tabulated in Table 2. A schematic of the above separation

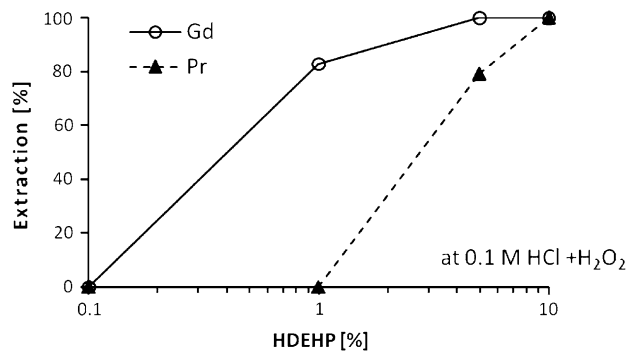
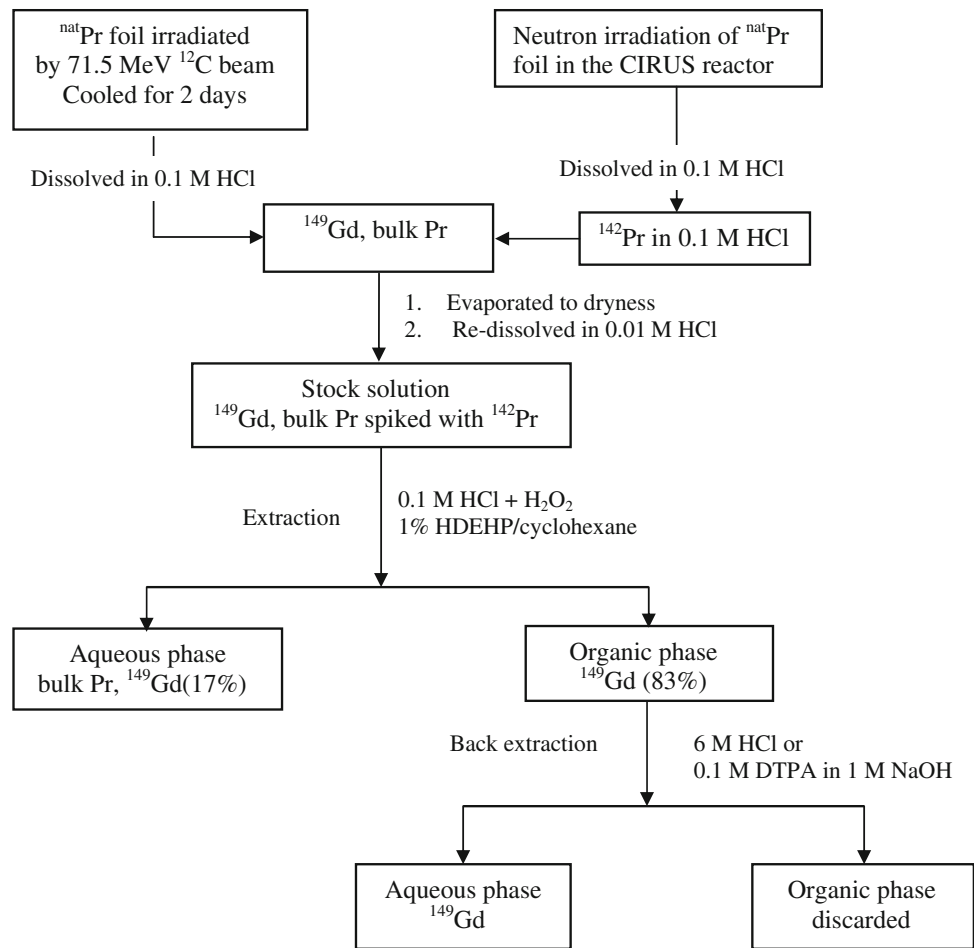


Fig. 5 Extraction profile of nca Gd and bulk Pr in LLX as a function of HDEHP concentration at a fixed strength of HCl (0.1 M) in presence of H_2O_2

Table 2 Distribution ratios (D) and corresponding separation factors (SF) at the optimal experimental conditions

LLX: experimental condition	D_{Gd}	D_{Pr}	SF(= $D_{\text{Gd}}/D_{\text{Pr}}$)
HCl (0.1 M)/HDEHP (1%)	3.7	0.04	93
HCl (0.1 M) + H_2O_2 / HDEHP (1%)	4.9	2×10^{-3}	2450

Fig. 6 Schematic presentation of the separation of nca Gd from natural Pr using LLX**Table 3** Comparison of D_{Gd} values and separation factors of the present work and earlier reported values

Optimal condition	Separation carried out between the pairs	D_{Gd}	S	Reference
0.1 M HCl + H ₂ O ₂ + 1% HDEHP	Gd (nca) and Pr (target)	4.9	$S_{\text{Gd/Pr}} = 2450$	This work
0.1 M HCl, 1% HDEHP	Gd (nca), Eu (co-produced nca product) and Pr (target)	1.8	$S_{\text{Gd/Pr}} = 240$ $S_{\text{Gd/Eu}} = 2.14$	[8]
0.0001 M HCl, 1% HDEHP	Gd (nca), CeO ₂ (target)	1.27	$S_{\text{Gd/Ce}} = 3340$	[7]
0.01 M HCl, 0.1% HDEHP	^{141}Ce , ^{153}Gd	4.9	$S_{\text{Gd/Ce}} = 155$	[6]

is presented in Fig. 6. The extraction patterns of nca Gd and bulk matrix are quite confirmative with our earlier publications [7, 8]. It is noteworthy to mention that addition of H₂O₂ improved D_{Gd} values and separation factor between nca Gd and bulk Pr compared to earlier works. A comparison of D_{Gd} and separation factor values with earlier experiments have been tabulated in Table 3. The contamination from ^{150}Gd (1.8 Myears) will be infinitesimally small due to very long half-life. In principle, presence of ^{151}Gd (120 days) is expected from the decay product of its precursor ^{151}Tb . However, no signature of ^{151}Gd was observed during radiochemical separation due to the low yield of ^{151}Tb and comparatively longer half-life of ^{151}Gd .

A finer adjustment in the target thickness may also reduce the production of impurity during irradiation.

Conclusion

Application of short-lived radionuclides requires reliable and faster method for the separation of desired lanthanide with high purity from the corresponding target matrix. The reported separation technique, which describes the separation of nca Gd from the bulk praseodymium target matrix by LLX using HDEHP requires about 80 min time. The indirect production of nca ^{149}Gd is advantageous compared

to earlier methods because of the following reasons (i) there are no co-produced nca radionuclides of other elements, therefore, high radiochemical purity for nca ^{149}Gd is achievable (e.g. reference [8], where ^{147}Eu was co-produced with nca Gd radionuclides) (ii) the present method also yields high radionuclidic purity for ^{149}Gd (e.g. reference [8], where both ^{147}Gd and ^{149}Gd were produced) (iii) due to the absence of any other co-produced radio-lanthanide, the separation scheme became easier. The reported method is simple, fast and reliable.

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