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Separation of ^{139}Ce using solvent extraction technique from La_2O_3 target irradiated by 14.7 MeV protons

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The radiochemical separation of no-carrier-added cerium from proton irradiated lanthanum was studied by solvent extraction using DEE, TBP and TPPO, the latter reagent being employed for the first time for separation of radiocerium from bulk of lanthanum. Distribution coefficients of cerium and lanthanum were investigated as a function of equilibrium time and concentration of HNO_3. A mixture of 0.05M $K_2Cr_2O_7$ and 0.1M H_2SO_4 was used as an oxidizing agent to improve the separation efficiency of cerium. A comparative study of the three extractants released that DEE is the best for separation of cerium from bulk of lanthanum oxide. The target was prepared by pressing. The production of ^{139}Ce of high radionuclidic purity and chemical purity via irradiation of lanthanum oxide target at MGC-20 cyclotron with protons of energy 14.5 MeV is described. The experimental yield was found to be 153 kBq/μA·h .

Introduction

Radionuclides are finding increasing applications in most branches of science and technology. The relatively long-lived radionuclide ^{139}Ce ($T_{1/2}$ = 137.6 d[1]) is useful as a standard for the calibration of γ-ray detectors. This radioisotope can be produced through ^{139}La(p, n)^{139}Ce with Q-value –1.06037 MeV and has only one strong γ ray of energy 165.857 keV[1] with 80% intensity, which is within the optimum energy range for detection with a gamma camera. Image degradation during single photon emission tomography (SPECT) due to attenuation and Compton scattering of photons can cause clinical image artifacts. DURAAN et al.[2] have shown that a ^{139}Ce line source can be used to determine attenuation maps for SPECT. The interest in this radionuclide is therefore increasing.

Two routes are feasible for the production of no-carrier-added ^{139}Ce, namely deuteron[3,4] and proton[5] irradiations of natural lanthanum ^{139}La (99.91%). Studies of chemical separation of cerium from lanthanum targets were previously investigated.[3–8] MAYER et al[6] used AG-X8 resin as anion exchanger for separation of radiocerium from lanthanum. The extraction of cerium in a tetravalent state from lanthanum was carried out using TBP,[7] di(2-ethyl-hexyl) orthophosphoric acid (HDEHP)[3,8] and diethyl ether (DEE).[4]

The aim of the present work is to produce ^{139}Ce of high radionuclidic purity from lanthanum cyclotron target via ^{139}La(p, n)^{139}Ce nuclear reaction. The emphasis was on improving the separation of cerium radionuclide in no-carrier added form. The separation in this work was carried out using three extractants namely DEE, TPPO, and TBP. Separation of ^{139}Ce from lanthanum target using the (TPPO) triphenyl phosphine oxide reagent has been carried out for the first time in this work.

Experimental

Chemicals and reagents

La_2O_3 (99.97%, Koch-light laboratories Ltd., England); triphenyl phosphine oxide (TPPO) obtained from Fluka Chemie GmbH, Germany; diethyl ether (DEE) obtained from Sisco research laboratories PVT-LTD Mumbai, India; and tributyl phosphate (TBP) from Schuchardt, Hohenbrun, Germany.

Instrumentation

For radioactivity measurement, a gamma-ray spectrometer consisting of HPGe detector connected to a multichannel analyzer and PC was used. The inactive content of the separated material was determined via inductively coupled plasma optical emission spectrometry (ICP-OES) using the system ULTIMA 2ICP, Jobin Yvon S. A., France.

Target and irradiation

The target material La_2O_3 in the form of powder was pressed under a pressure of 10 tons.f/cm^2 to 13 mm diameter pellet. The pellet was covered with a high-purity Al-foil of 10 μm thickness. The irradiation was preformed at MGC-20 cyclotron available in Egypt with beam current of 1 μA , irradiation time five hours and at incident proton energy of 14.5 MeV. During the irradiation the sample was cooled at the back by circulating water.

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Determination of radionuclidic purity, chemical purity and yield measurement

The radionuclidic purity and the absolute yield of ^{139}Ce were determined by γ-ray spectroscopy. The peak area analysis was done using the software Gamma-vision (Version 5.1, EG&G ORTEC). The decay data[1] of the radionuclide concerned is given in Table 1. Measurements of the absolute photopeak detection efficiency as a function of energy were carried out with calibrated γ-ray standard sources of ^{133}Ba, ^{60}Co, ^{137}Cs, ^{22}Na and ^{154}Eu. The total uncertainty in the yield measurement was obtained by summing the squares of the individual uncertainties (%) and taking the square root of the sum. The major individual uncertainties were: detector efficiency (5–10%) and peak area determination (2–5%). The total uncertainties for the radionuclide yield was 6–12%. The chemical impurity in the separated radiocerium was measured against lanthanum using ICP.

Separation of ^{139}Ce from irradiated lanthanum target

For determination of the distribution coefficients, a stock solution of the activated sample was prepared by dissolving the irradiated matrix in a mixture of 5 mL conc. HNO_3 and 5 mL of H_2O_2. The solution was evaporated to incipient dryness, and the residue was dissolved in 50 mL of 1M HNO_3. To 1 mL of the solution containing the activity and lanthanum target, a mixture of 1 mL of 0.5M $K_2Cr_2O_7$ and 1 mL of 1M H_2SO_4 as oxidizing agent was added. To obtain the desired molarity in a total volume of 10 mL, nitric acid was added to the mixture. The solution was transferred to a separating funnel and subjected to gentle shaking with an equal volume of each 30% (v/v) TBP diluted in chloroform, 3% (w/v) TPPO dissolved in chloroform and DEE. After disengagement, both aqueous and organic phases were monitored by γ-ray spectrometer and ICP, to calculate the distribution coefficients of cerium and lanthanum, respectively.

Results and discussion

The predominant radionuclide present in the irradiated target in the energy window $E_p = 14.5 \rightarrow 10$ MeV was ^{139}Ce (Fig. 1). The procedure of chemical separation of cerium from lanthanides depends on the oxidation of cerium to the +4 state[4]. The radiochemical separation of no-carrier-added radiocerium from bulk of lanthanum was attempted via solvent extraction using three extractants: DEE, TBP and TPPO. The details of the separation are given in the following.

Table 1. Characteristics of radionuclide formed in irradiation of La_2O_3 target*

Nuclear reaction	Q-value, MeV	Product nuclide	$T_{1/2}$	Energies of principal γ-rays, keV (Intensity, %)
(p, n)	–1.06037	^{139}Ce	137.6 d	165.8 (80)

* The target ^{139}La is monoisotopic.

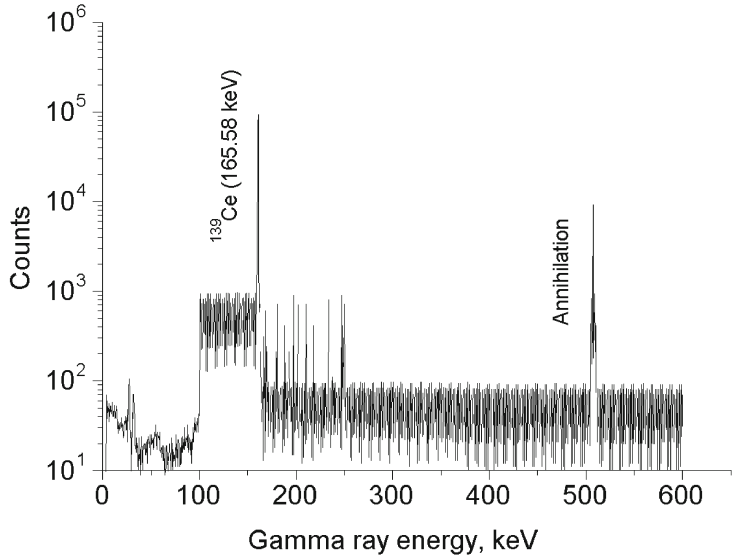

Fig. 1. Gamma-ray spectrum of $^{nat}La_2O_3$ target irradiated with 14.5 MeV protons

Equilibrium time

The extraction kinetics of no-carried-added cerium was studied for the three extractants. Figure 2 shows that the variation of the extraction behavior depends on the time of contact between aqueous and organic phases. It was found that after about 3 min of shaking time, the equilibrium was attained.

Extraction behavior of no-carrier-added ^{139}Ce using DEE

The extraction coefficients of no-carrier-added Ce(IV) and bulk of La(III) were studied over a wide range of nitric acid concentration (2–11M), the results are illustrated in Fig. 3. The distribution coefficient (K_d) of ceric nitrate increases with increasing nitric acid concentration, reaches a maximum value at 9M HNO_3 and then gradually decreases. On the other hand the trivalent La did not display any extraction over the same range of acidity. Hence the optimum concentration of HNO_3 for the separation of radiocerium from lanthanum target is 9M.

For back-extraction of radiocerium from the organic phase, at HNO_3 concentration below 3M cerium has an observable low K_d-value that allows for back-extraction. It is also necessary to enhance the back extraction by reduction of Ce(IV) to Ce(III) state. Therefore a mixture of 1M HNO_3 and 30% of H_2O_2 was tested for this purpose; the back-extraction efficiency amounted to 87% of initial activity.

Extraction behavior of no-carrier-added ^{139}Ce using TBP

The extraction behavior of no-carrier-added Ce(IV) and bulk of La(III) within the range of nitric acid concentration from 2 to 11M are illustrated in Fig. 4. Radiocerium and lanthanum globally have the same behavior as in the case of DEE. The only difference is that the distribution coefficient of no-carrier-added cerium using TBP increases with the increasing nitric acid concentration till it reaches a maximum value at 6M nitric acid, after that it decreases again. As mentioned before for back-extraction of no-carrier-added cerium from organic phase containing TBP-Ce complex, a mixture of 1M HNO_3 and 30% of H_2O_2 was used. The efficiency of separation reached a value of 92.5% relative to the initial activity.

Extraction behavior of no-carrier-added ^{139}Ce using TPPO

Figure 5 shows the relation between the distribution coefficient of no-carrier-added Ce(IV) in the presence of a bulk of La(III) as a function of nitric acid concentration using the TPPO as an extractant for the first time. It is clear that the K_d value of radiocerium increases within the acidity range of 2 to 6M and then decreases again over the acidity range of 7 to 11M. The extracion behavior of no-carrier-added cerium(IV) is similar to that of no-carrier-added radiozirconium(IV) using 3% TPPO in chloroform reported by KANDIL et al.[9] In the same manner carrier-added lanthanum had negligible extractability by TPPO over the acidity range of 2 to 11M, as in the case of carrier-added yttrium(III).[9] Also as mentioned before for back-extraction of no-carrier-added cerium from organic phase containing TPPO-Ce complex, a mixture of 1M HNO_3 and 30% of H_2O_2 was used. 85.5% separation efficiency relative to that of initial activity was achieved.

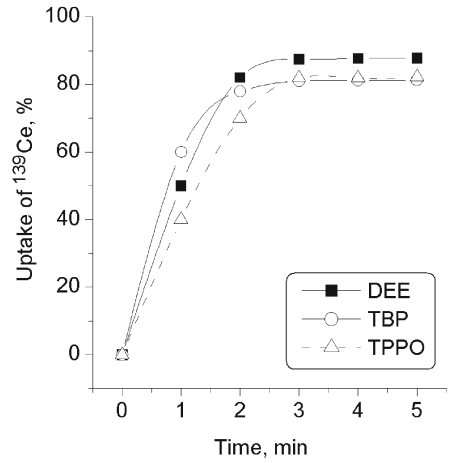

Fig. 2. Uptake of radiocerium (%) in the first extraction as a function of contact time with three extractants

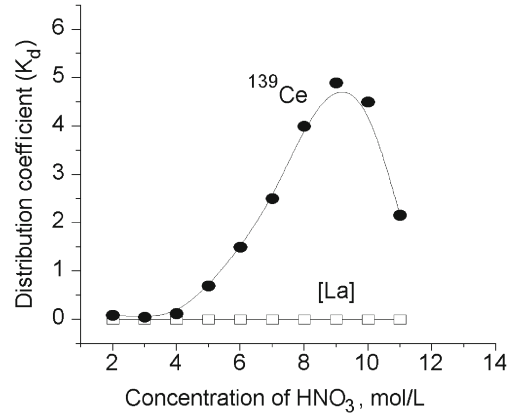

Fig. 3. Distribution coefficients of ^{139}Ce and La versus HNO_3 concentration over the range of 2–11M, using DEE, shaking time 3 minutes

Comparison of investigated methods for the separation of radiocerium

A summary of the results of the three investigated methods for the separation of no-carrier-added radiocerium from proton irradiated La_2O_3 target using DEE, TBP and TPPO is given in Table 2. Regarding the DEE, it is observed that only 0.5% of lanthanum was extracted from 9M nitric acid. On the other hand TPPO extracted as much as 2.7% of lanthanum from 6M nitric acid. The extractant TBP displays a higher efficiency of separation but also high extraction of lanthanum of 4.1%. Again with regard to DEE, further washing of organic phase improved the chemical purity of radiocerium (Table 3). This improvement is due to the low K_d of La-DEE (less than 10^{-4}) in 9M of HNO_3–DEE system. The non-specified extracted species of La were easily stripped from the organic phase with a new portion of 9M HNO_3. On the other hand, no improvement in chemical purity was achieved by further washing. This may be referred to the high K_d values of La-TBP and of La-TPPO in 6M of HNO_3–TBP system and in 6M of HNO_3–TPPO system which ranges between 0.2–0.4, that reflects a slight specific extraction. We have to mention that improvement of chemical purity by further washing is normally accompanied by a loss in activity. Generally, out of the three extractants, DEE is the best one for obtaining high-purity no carrier added cerium in the nitrate form.

Optimum conditions for separation of ^{139}Ce

The flow sheet of the optimized method of separation of no-carrier-added radiocerium from proton irradiated La_2O_3 target is given in Fig. 6. The target was dissolved in a mixture of 5 mL of conc. HNO_3 plus 5 mL of H_2O_2 while heating at 100 °C. The solution was evaporated to incipient dryness, and the residue was dissolved in 10 mL of a mixture of 9M HNO_3 plus 0.05M $K_2Cr_2O_7$ and 0.1M H_2SO_4 and the solution was transferred to a separatory funnel. The reaction vessel was rinsed with new 10 mL of the same mixture and the solution was also transferred to the funnel. Thereafter 20 mL of DEE were added to it and the mixture was shaken for 3 min. The extraction process was repeated using a new portion of DEE. The two organic phases containing radiocerium were combined and first scrubbed with 10 mL of above mixture. Then 15 mL of 1M HNO_3 plus 5 mL of 30% H_2O_2 was added to the organic phase and the whole mixture was shaken for 3 min. This step was repeated with a new portion of 1M HNO_3 plus 30% H_2O_2.

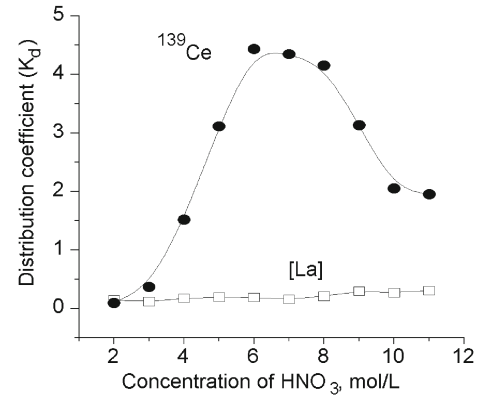

Fig. 4. Distribution coefficients of ^{139}Ce and La versus HNO_3 concentration over the range of 2–11M, using TBP, shaking time 3 minutes

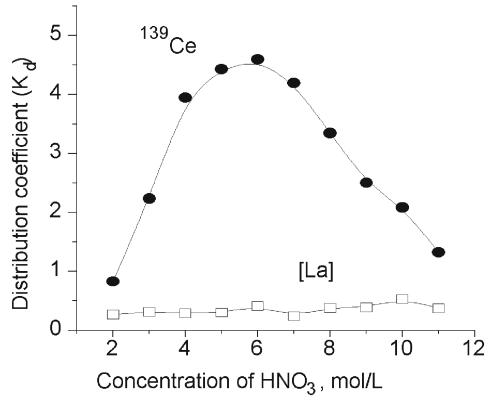

Fig. 5. Distribution coefficients of ^{139}Ce and La versus HNO_3 concentration over the range of 2–11M, using 3% TPPO in chloroform, shaking time 3 minutes

The optimized separation method reported above was used practically in the production of ^{139}Ce via the ^{139}La(p, n)^{139}Ce reaction. In this case a La_2O_3 pellet was irradiated with 14.5 MeV protons for 5 h at 1 μA. The chemical separation of ^{139}Ce was done about one day after the end of bombardment (EOB). The results are summarized in Table 4. The experimentally obtained batch yield of ^{139}Ce is sufficient for tracer studies. However, the yield could be further increased. The target[10] could withstand currents up to 10 μA and the irradiation time could be increased to about 10 h. It is thus possible to increase the batch yield of the radionuclide under consideration by a factor of about 20.

Table 2. Comparison of separation methods for no-carrier-added cerium from La_2O_3 target irradiated with protons

Extractant	Nitric acid concentration, M	Efficiency of separation, %	Extraction efficiency of La, %
DEE	9	87	0.5
TPPO	6	85.5	2.7
TBP	6	92.5	4.1

Table 3. Effect of washing time for organic phase on the efficiency of separation of no-carrier-added ^{139}Ce from La_2O_3 target irradiated with protons

	Separation efficiency of ^{139}Ce, %			Extraction efficiency of La, %		
Number of washing	0	1	2	0	1	2
DEE	87	68	30	0.5	0.002	0.000
TPPO	85.5	70	20	2.7	2.7	2.6
TBP	92.5	80	50	4.1	4.0	4.0

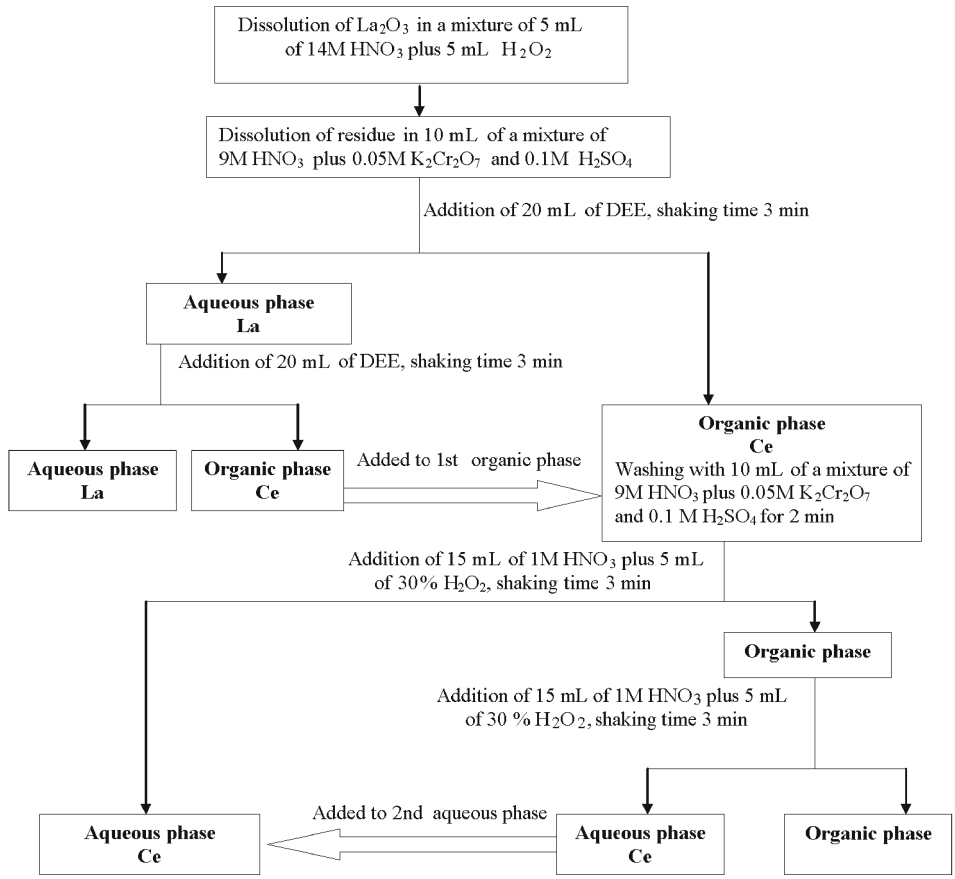

Fig. 6. Flow sheet of separation of ^{139}Ce from La_2O_3-target

Table 4. Thick target yield of ^{139}Ce

Proton energy range within the target, MeV	Irradiation parameters	Theoretical yield of ^{139}Ce radionuclide at EOB, kBq	Batch yield of radionuclide at EOB, kBq
$E_p = 14.5 \rightarrow 10$	1 μA, 5 h	1295	762

Production yields

A comparison of the practical yield with the theoretical yield was also undertaken. The excitation function of the ^{139}La(p, n)^{139}Ce reaction has been recently measured in our group[11] and elsewhere.[5] We adopted our own data that have been done in our cyclotron MGC-20, because they appeared to us to be more consistent. Using those data we calculated the thick target yield[12] of ^{139}Ce from a La_2O_3 target for the respective energy ranges used in the experiment. In this connection the range-energy relationship given by WILLIAMSON et al.[13] was used. The theoretical yield thus obtained was compared with the experimental batch yield. We found that the experimental yield of ^{139}Ce amounted to 86.6% of the theoretical value before starting the chemical separation process but after the separation of ^{139}Ce from lanthanum oxide target the experimental yield was 59% of the theoretical value. Considering the various factors affecting the experimental yields[14] (uncertainty in the beam current measurement, radiation damage effect, beam energy, etc.), the results appear to be satisfactory. Moreover, as mentioned before, further washing in the chemical separation process is an effective factor in activity losses. An experimental yield of 153 kBq/μA·h in correlation with that obtained by OCHAB and MISIAK[4] was achieved. Therefore the experimental yield in this work suggests that the production process followed is satisfactory and reliable.

Conclusion

The separation of no-carrier-added cerium from proton-irradiated lanthanum by solvent extraction using DEE is superior relative to the other investigated extractants. The chemical purity of the product was improved by further washing. In this work the major loss in activity happened during the separation process of ^{139}Ce from lanthanum oxide target. The achieved batch yield of the radionuclide ^{139}Ce was about 153 kBq/μA·h.

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