Production of no-carrier-added ^{89}Zr at an 18 MeV cyclotron, its purification and use in investigations in solvent extraction

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Abstract

The chemical separation of zirconium from lanthanides by liquid–liquid extraction is challenging but critical for medical and technological applications. Using the example of ^{89}Zr , we optimize the liquid–liquid-extraction process by means of the radiotracer technique. We produced ^{89}Zr by proton irradiation of a metallic yttrium target at a cyclotron. The purification of the radionuclide was performed by a UTEVA resin. ^{89}Zr was separated in no-carrier-added form in a sulfuric acid solution. ^{89}Zr was successfully used in solvent extraction tests with calixarenes for the separation of zirconium from lanthanides. This reaction is suitable for the efficient extraction and purification of lanthanides.

Keywords Zirconium-89 · Solvent extraction with calixarenes · Natural yttrium-89 target · Proton induced nuclear reaction · Chemical separation

Introduction

The zirconium-89 radionuclide is widely used radiotracer in different fields of interest. Medical applications include immuno imaging, cell imaging, tumor cell therapy, antibody imaging and pharmacokinetics [1–6]. In geochemical and environmental studies zirconium-89 is used as a surrogate for tetravalent actinides e.g. in the field of aqueous chemistry, surface chemistry, migration behavior in nuclear waste repositories, thermodynamics, kinetics [7–10].

The motivation of the present work is the development of methods for the extraction and purification of lanthanides within the ore processing. The processing and separation of the ore leachates is a challenging and expensive process due to the similarity of the chemical and physical properties of the lanthanides and the contaminants. This study focuses on the utilization of calixarenes as highly selective and cost effective extracting agent for the separation of zirconium and lanthanides from ore leachates by means of liquid/liquid extraction. Calixarenes are cyclic organic

macromolecules, have a cage structure and can act as a host for guest ions, depending on pH and the ion size [11–15]. Zr is a likely major contaminant of the lanthanides and also acts as surrogate for the ore-associated tetravalent actinides [16, 17]. The use of the radiotracer zirconium-89 allows for the easy access to the highly complex system. Without extensive sample preparation a detailed quantification of Zr and kinetic studies become possible and allow the optimization and parameterization of the chemical-technological process.

^{89}Zr decays by positron emission ($T_{1/2} = 78.41$ h, $I_{\beta+} = 22.74\%$, $E_{\beta+, \text{end-point}} = 902$ keV) and by electron capture (77.26%, $I_{\gamma} = 99.04\%$, $E_{\gamma} = 909.15$ keV) to stable ^{89}Y [18]. Several nuclear reactions, mainly in order to produce ^{89}Zr as a theragnostic radionuclide have been published. Possible nuclear reactions are discussed: $^{89}\text{Y}(\text{p}, \text{n})^{89}\text{Zr}$, $^{89}\text{Y}(\text{d}, 2\text{n})^{89}\text{Zr}$, $^{\text{nat}}\text{Zr}(\text{p}, \text{pxn})^{89}\text{Zr}$, $^{\text{nat}}\text{Sr}(\alpha, \text{xn})^{89}\text{Zr}$ and $^{90}\text{Zr}(\text{n}, \text{xn})^{89}\text{Zr}$ [19–33]. In the present study, ^{89}Zr was produced at an in-house cyclotron via the nuclear reaction $^{89}\text{Y}(\text{p}, \text{n})^{89}\text{Zr}$. By utilizing ion exchange chromatography techniques, we investigate purification processes using UTEVA resin material [34]. Specifically, we analyze the purification efficiency.

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Experimental

Material and methods

The yttrium foil with natural isotope composition (100% ^{89}Y) was purchased from Goodfellow (Germany). The target aluminium plate (AlMg3, Stahl Center Leipzig, Germany) and the aluminium foil (Goodfellow, Germany) had a purity of 96.2 and 99.999%, respectively. The UTEVA Resin was purchased from TrisKem International (France) with a grain size of 50 μm –100 μm [35]. The calixarenes 5,11,17,23-Tetrakis-*p*-tert-butyl-25,27-bis[3-diethoxyphosphoryl]-propoxy]-26,28-bis(carboxymethoxy)-calix[4]arene (**L**₁) and 5,11,17,23-Tetra-*p*-tert-butyl-25,27-bis[(8-hydroxyquinoline-carbaldehyde-hydrazone-carbonylmethoxy)]-26,28-dihydroxy-calix[4]arene (**L**₂) were synthesized and characterized (NMR, IR, UV/Vis and ESI-MS) at the Institut für Anorganische Chemie (Universität Leipzig, Germany), respectively (see Fig. 1) [36, 37]. These calixarenes were chosen due to the prediction of their high complex stability constants.

All other chemicals used were obtained from Sigma-Aldrich, Merck and Fluka. All solutions were prepared with deionized water of a resistivity not less than 18.2 M Ω /cm. An ICP-MS (inductively coupled plasma mass spectrometer, Element XR, Thermo Scientific, UK) was used in preliminary tests with the non-radioactive material. γ -ray spectroscopy was performed with an ORTEC detector (dspec pro, GEM-40190P, GammaVision A66-B32, Germany). The detector was calibrated with a ^{152}Eu standard (PTB 443–88, PTB, Germany) in the energy range from 50 to 1500 keV. The fractions of the solvent extraction were measured with a γ -counter (Wizard 3'', PerkinElmer, Germany) at 909.15 keV, which was also calibrated with the ^{152}Eu standard.

Irradiation

The Y target was prepared by inserting an yttrium foil (12.5 mm $\times$ 12.5 mm, 150 μm thick) in a cavity of an aluminium plate with a diameter of 13 mm and a depth of 150 μm . The foil was mechanically fixed by imposing a 2 mm thick aluminium frame. The proton irradiation was performed at our in-house cyclotron “Cyclone 18/9@” (IBA Molecular, Belgium) with a Nirta@Solid target irradiation station (IBA Molecular, Belgium). The maximal current was 22 μA (mean 19 μA) at 18 MeV proton energy on the complete target system. A 12.5 μm titanium window was used to separate the high vacuum system from the helium cooling system. Additionally, the target was cooled with water on its backside (13 $^{\circ}\text{C}$). The yttrium foil was covered with a 900 μm aluminium foil, where the nuclear reactions $^{89}\text{Y}(\text{p},2\text{n})^{88}\text{Zr}$ and $^{89}\text{Y}(\text{p},\text{pn})^{88}\text{Y}$ should not be in consideration ($E_{\text{p}} < 11.7$ MeV) due to their high threshold energy (Table 1) [25, 28]. The exit proton energy was calculated as ~ 10.1 MeV at the end of the target material. The irradiation time was 70 min. As a byproduct, $^{89\text{m}}\text{Zr}$ ($T_{1/2} = 4.16$ min) was produced by the nuclear reaction $^{89}\text{Y}(\text{p},\text{n})^{89\text{m}}\text{Zr}$ (Table 1) [18, 21]. After decay of the short-lived radionuclide $^{89\text{m}}\text{Zr}$ for 60 min the irradiated yttrium foil was quantitatively dissolved in 2 mL concentrated HNO_3 . This solution was evaporated to dryness.

Chemical separation of ^{89}Zr

The dried $\text{Y}(\text{NO}_3)_3$ with ^{89}Zr was dissolved in 2 mL 9 M HNO_3 (Fig. 2). The UTEVA resin was triple preconditioned with 2 mL 9 M HNO_3 . The prepacked column had a length of 26 mm and a diameter of 10 mm and was filled with 0.80 g (density 0.39 g/mL) of the resin. The 2 mL $\text{Y}/^{89}\text{Zr}$ solution was passed through the column by using a syringe at a flow of ~ 0.6 mL/min. The adsorbed ^{89}Zr was washed five times with 2 mL 9 M HNO_3 (fractions 1–6).

Fig. 1 Molecular structures of the calixarenes **L**₁ and **L**₂ [36, 37]

Table 1 Possible radionuclides produced during irradiation of ^{nat}Y with protons below 11.7 MeV [18, 25]

Nuclide	Half-life	Decay mode (%)	E_γ (keV)	I_γ (%)	Contributing reactions	$E_{\text{threshold}}$ (MeV)
^{89g}Zr	78.41 h	EC + β^+ (100)	909.1 511.0	99.04 45.50	$^{89}\text{Y}(\text{p},\text{n})$ IT decay of ^{89m}Zr	3.6560
^{89m}Zr	4.16 m	IT to ^{89g}Zr (93.77) EC + β^+ to stable ^{89}Y (6.23)	587.8 1507.4	89.62 6.06	$^{89}\text{Y}(\text{p},\text{n})$	3.6560
^{88g}Zr	83.4 d	EC (100)	392.9	97.29	$^{89}\text{Y}(\text{p},2\text{n})$	13.0787
^{88g}Y	106.63 d	EC + β^+ (100)	1836.1 898.0	99.20 93.70	$^{89}\text{Y}(\text{p},2\text{n})^{88g}\text{Zr} \rightarrow ^{88}\text{Y}$	13.0787

Fig. 2 Scheme for the separation of ^{89}Zr from the irradiated ^{nat}Y target

To optimize the Y/Zr separation, preparatory experiments with non-radioactive Y/Zr mixtures were measured by ICP-MS. Finally, the ^{89}Zr was eluted from the resin with 6 bed column volumes of 0.1 M oxalic acid (fractions 7–12). All fractions (2 mL) were measured using γ -ray spectroscopy for determining the ^{89}Zr (909.15 keV) content. The combined Zr-solutions were evaporated to dryness, fumed with a few drops of concentrated H_2SO_4 to get rid of the oxalic acid, and the ^{89}Zr was dissolved four times with 250 μL 1 M H_2SO_4 (1 mL in sum). The radionuclide purity was determined by γ -ray spectroscopy and the quantification of the amount of ^{89}Zr in this solution was achieved by measuring the 909.15 keV-peak. The detection limit was 30 Bq/mL at the energy of 909.15 keV.

Solvent extraction with calixarenes

The calixarenes **L**₁ or **L**₂ were dissolved in chloroform to give a solution of 100 μM . The aqueous solution were prepared by adding ~ 5 kBq/mL ^{89}Zr to a non-radioactive Zr-solution (10 μM $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) at the desired pH (1–5) in diluted H_2SO_4 . 3 mL of the aqueous solution was shaken with 3 mL of the organic phase in a stoppered vial on a

horizontal shaker at 300 min^{-1} . The phases were allowed to equilibrate for 60 min. After separation of the phases for 1 min, an aliquot of 2 mL of the aqueous phase were measured by γ -counting in comparison to 2 mL of the aqueous solution before extraction. The percentage extraction %E was calculated by means of the two activities ($A_{\text{initial}} = ^{89}\text{Zr}$ in aqueous solution before extraction, $A_{\text{final}} = ^{89}\text{Zr}$ in aqueous solution after extraction) by using the Eq. (1)

$$\%E = 100 \cdot \frac{[A_{\text{initial}} - A_{\text{final}}]}{[A_{\text{initial}}]} \quad (1)$$

The distribution coefficient D can be calculated by Eq. (2).

$$D = (100 / \%E - 1)^{-1} \quad (2)$$

Results and discussion

Preparation of ^{89}Zr : The separation efficiency of ^{89}Zr from the Y target by chromatography is shown in Fig. 3. Y is washed from the resin within the first 5 fractions (1–6 in Fig. 3) with 9 M HNO_3 . ^{89}Zr and the non-radioactive Zr were eluted within the first oxalic acid fraction (7–12 in Fig. 3). No ^{89}Zr could be found in the HNO_3 fractions with a detection limit of 30 Bq/mL. Fraction 7 was evaporated and the residue was fumed to dryness with sulfuric acid. The ^{89}Zr was dissolved in dilute sulfuric acid and was used for the solvent extraction tests. The radioactivity was measured and calculated to be $414 \text{ MBq} \pm 20 \text{ MBq}$ (25.7 MBq/ μAh) at the end of the irradiation. The dissolution of the irradiated target, the separation of ^{89}Zr and the fuming with sulfuric acid are performed within ~ 6 h.

Application of ^{89}Zr : After adding the radiotracer to a non-radioactive Zr solution, the solvent extraction behaviour with **L**₁ and **L**₂ was tested between pH 0.15 and pH 4. Figure 4 illustrates the strong pH dependence on Zr extraction independently of which calixarene is used. The extraction at pH 4 is between 90–95% for both calixarenes. In comparison to an experiment with Eu^{3+} [36], it is possible to separate Zr from the lanthanides in the region

Fig. 3 Chromatographic separation of irradiated Y and ^{89}Zr with UTEVA resin; elution of Y and washing of the adsorbed ^{89}Zr with 9 M HNO_3 (fractions 1–6); elution of ^{89}Zr with 0.1 M oxalic acid (fractions 7–12); 2 mL each fraction; flux 0.6 mL/min; comparison of a non-radioactive solution (80 mg/L Y; 1 mg/L Zr) measured by ICP-MS and the radiochromatogram with 414 MBq ^{89}Zr

Fig. 4 Solvent extraction of $[\text{}^{89}\text{Zr}]\text{Zr}$ with the calixarenes L_1 (circles) and L_2 (squares) in dependence on pH. Comparison with $[\text{}^{152}\text{Eu}]\text{Eu}^{3+}$ and L_2 (triangles) [36]

of pH ~ 3.5 (Fig. 4). The $\text{pH}_{1/2}$ values (50% extraction of the elements) are 2.5 and 5.0 for Zr and Eu, respectively. Consequently, we established a protocol for the purification of the lanthanides from a Zr contamination, involving adjustment of the pH first to pH ~ 3.5 , followed by reextraction of Zr at pH ~ 0.25 . Afterwards the lanthanides are be extracted with the identical calixarene solution at higher pH values (6–7) from the other contaminants in the ore leachates, e.g. iron and aluminium.

Summary and conclusions

A fast and quantitative method for the production and purification of ^{89}Zr was implemented at our research site, and enables a prompt availability of ^{89}Zr . Within a single day it is possible to irradiate a few mg-scale Y foils and separate the radionuclide ^{89}Zr with UTEVA resin in a no-carrier-added solution in the range of a few hundred MBq/mL concentration range with a radiochemical yield of $100\% \pm 8\%$ ($n = 3$) and a radionuclide purity $> 99\%$. For investigation in solvent extraction with calixarenes, ^{89}Zr was used as radiotracer to optimize the separation from lanthanides. The fast availability of ^{89}Zr provides the opportunity for studying multiple natural and technical systems, including geochemical behavior and ore processing, the mobility of Zr-nanoparticles and medical application methods.

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Compliance with ethical standards

Conflict of interest The authors declare that there is no conflict of interest.

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References

1. Das SS et al (2017) Production and radiochemical separation of a potential immuno-PET imaging agent ^{89}Zr from proton irradiated ^{nat}Y target. J Radioanal Nucl Chem 313:641–645. <https://doi.org/10.1007/s10967-017-5316-9>
2. Sato N et al (2015) ^{89}Zr Oxine Complex PET Cell Imaging in Monitoring Cell-based Therapie. Radiology 275:490–500. <https://doi.org/10.1148/radiol.15142849>

3. Walther M et al (2011) Implementation of ^{89}Zr production and in vivo imaging of B-cells in mice with ^{89}Zr -labeled anti-B-cell antibodies by small animal PET/CT. *Appl Radiat Isot* 69(6):852–857
4. Deri MA et al (2013) PET imaging with ^{89}Zr : From radiochemistry to the clinic. *Nucl Med Biol* 40:3–14. <https://doi.org/10.1016/j.nucmedbio.2012.08.004>
5. Verel I et al (2003) ^{89}Zr Immuno-PET: Comprehensive Procedures for the Production of ^{89}Zr -Labeled Monoclonal Antibodies. *J Nucl Med* 44:1271–1281
6. Kasbollah A et al (2013) Review on Production of ^{89}Zr in a Medical Cyclotron for PET Radiopharmaceuticals. *J Nucl Med Technol* 41:35–41. <https://doi.org/10.2967/jnmt.112.111377>
7. Altmair M et al (2013) Recent Advances in Aqueous Actinide Chemistry and Thermodynamics. *Chem Rev* 113:901–943. <https://doi.org/10.1021/cr300379w>
8. Holliday KS et al (2011) Environmental behavior of ZrO_2 -MgO ceramics containing UO_2 . *Radiochim Acta* 99:799–806. <https://doi.org/10.1524/ract.2011.1884>
9. Pin C, Joannon S (2002) Combined cation-exchange and extraction chromatography for the concomitant separation of Zr, Hf, Th, and the Lanthanides from geological materials. *Talanta* 57:393–403. [https://doi.org/10.1016/S0039-9140\(02\)00040-1](https://doi.org/10.1016/S0039-9140(02)00040-1)
10. Raslan MF, El-Feky MG (2012) Radioactivity and mineralogy of the altered granites of the Wadi Ghadir shear zone, South Eastern Desert. *Egypt Chin J Geochem* 31:30–40. <https://doi.org/10.1007/s11631-012-0546-6>
11. Mohhtari B et al (2011) A review of calixarene applications in nuclear industries. *J Radioanal Nucl Chem* 287:921–934. <https://doi.org/10.1007/s10967-010-0881-1>
12. Arnaud-Neu F et al (1999) Extraction and Complexation of Alkali, Alkaline Earth, and f-Element Cations by Calixaryl Phosphine Oxides. *Chem Eur J* 5:175–186. [https://doi.org/10.1002/\(SICI\)1521-3765\(19990104\)5:1%3C175::AID-CHEM175%3E3.0.CO;2-P](https://doi.org/10.1002/(SICI)1521-3765(19990104)5:1%3C175::AID-CHEM175%3E3.0.CO;2-P)
13. Bauer A et al (2019) Multidentate extracting agents based on calix[4]arene scaffold – $\text{U}^{\text{VI}}/\text{Eu}^{\text{III}}$ separation studies. *Sep Purif Technol* 213:246–254. <https://doi.org/10.1016/j.seppur.2018.12.041>
14. Huang H et al (2014) Extraction of trivalent americium and europium from nitric acid solution with a calixarene-based diglycolamid. *Sep Purif Technol* 123:235–240. <https://doi.org/10.1016/j.seppur.2013.12.039>
15. Lu X et al (2017) Reactive extraction of europium(III) and neodymium(III) by carboxylic acid modified calixarene derivatives: Equilibrium, thermodynamics and kinetics. *Sep Purif Technol* 188:250–259. <https://doi.org/10.1016/j.seppur.2017.07.040>
16. Voncken, J. H. L., 2016. The Rare Earth Elements, first ed., SpringerBriefs in Earth Sciences, ebook. <https://www.springer.com/de/book/9783319268071>
17. Eichholz GG et al (1953) The determination of uranium and thorium in ores. *Can J Phys* 31:613–628. <https://doi.org/10.1139/p53-058>
18. NuDat 2.7 database. 2015. <https://www.nndc.bnl.gov/nudat2/> (accessed 22 April 2020).
19. Sadeghi M et al (2012) Accelerator production of the positron emitter zirconium-89. *Ann Nucl Energy* 41:97–103. <https://doi.org/10.1016/j.anucene.2011.11.014>
20. Kandil SA et al (2007) A comparative study on the separation of radiozirconium via ion-exchange and solvent extraction techniques, with particular reference to the production of ^{88}Zr and ^{89}Zr in proton induced reactions on yttrium. *J Radioanal Nucl Chem* 274:45–52. <https://doi.org/10.1007/s10967-006-6892-2>
21. Uddin MS et al (2005) Experimental studies on excitation functions of the proton-induced activation reactions on yttrium. *Appl Radiat Isot* 63:367–374. <https://doi.org/10.1016/j.apradiso.2005.04.006>
22. Yang S et al (2017) Production cross sections of proton-induced reactions on yttrium. *Nucl Instr Meth B* 398:1–8. <https://doi.org/10.1016/j.nimb.2017.03.021>
23. Sharifian M et al (2017) Modeling and experimental data of zirconium-89 production yield. *Appl Radiat Isot* 130:206–210. <https://doi.org/10.1016/j.apradiso.2017.09.044>
24. Omara HM et al (2009) Proton induced reactions on ^{89}Y with particular reference to the production of the medically interesting radionuclide ^{89}Zr . *Radiochim Acta* 97:467–471. <https://doi.org/10.1524/ract.2009.1645>
25. Khandaker MU et al (2012) Investigations of $^{89}\text{Y}(p, x)^{86,88,89}\text{Zr}$, $^{86\text{m}+g,87g,87\text{m},88g}\text{Y}$, ^{85}gSr , and ^{84}gRb nuclear processes up to 42 MeV. *Nucl Instr Meth B* 271:72–81. <https://doi.org/10.1016/j.nimb.2011.11.009>
26. Steyn GF et al (2011) Excitation Functions of Proton Induced Reactions on ^{89}Y and ^{93}Nb with Emphasis on the Production of Selected Radio-Zirconiums. *J Korean Phys Soc* 59:1991–1994. <https://doi.org/10.3938/jkps.59.1991>
27. Mustafa MG et al (1988) Measurements and a direct-reaction-plus-Hauser-Feshbach analysis of $^{89}\text{Y}(p, n)^{89}\text{Zr}$, $^{89}\text{Y}(p, 2n)^{88}\text{Zr}$, and $^{89}\text{Y}(p, p^n)^{88}\text{Y}$ reactions up to 40 MeV. *Phys Rev C* 38:1624–1637. <https://doi.org/10.1103/PhysRevC.38.1624>
28. Zweit J et al (1991) Production of no-carrier-added zirconium-89 for positron emission tomography. *Appl Radiat Isot* 42:199–201. [https://doi.org/10.1016/0883-2889\(91\)90074-B](https://doi.org/10.1016/0883-2889(91)90074-B)
29. Tang Y et al (2016) A simple and convenient method for production of ^{89}Zr with high purity. *Appl Radiat Isot* 118:326–330. <https://doi.org/10.1016/j.apradiso.2016.09.024>
30. Uddin MS et al (2008) Excitation functions of the proton induced nuclear reactions on natural zirconium. *Nucl Instr Meth B* 266:13–20. <https://doi.org/10.1016/j.nimb.2007.10.010>
31. Kandil SA et al (2007) Excitation functions of (α, xn) reactions on ^{nat}Rb and ^{nat}Sr from threshold up to 26 MeV: Possibility of production of ^{87}Y , ^{88}Y and ^{89}Zr . *Appl Radiat Isot* 65:561–568. <https://doi.org/10.1016/j.apradiso.2006.12.007>
32. Ivanov PI et al (2014) Cyclotron production and radiochemical purification of $^{88,89}\text{Zr}$ via α -particle induced reactions on natural strontium. *Appl Radiat Isot* 90:261–264. <https://doi.org/10.1016/j.apradiso.2014.04.018>
33. Lewis VE, Zieba KJ (1980) A transfer standard for d + t neutron fluence and energy. *Nucl Instr Meth* 174:141–144. [https://doi.org/10.1016/0029-554X\(80\)90422-X](https://doi.org/10.1016/0029-554X(80)90422-X)
34. Kazakov AG et al (2018) Separation of ^{89}Zr from irradiated yttrium targets by extraction chromatography. *J Radioanal Nucl Chem* 317:605–611. <https://doi.org/10.1007/s10967-018-5888-z>
35. Horwitz EP et al (1992) Separation and preconcentration of uranium from acidic media by extraction chromatography. *Anal Chim Acta* 266:25–37. [https://doi.org/10.1016/0003-2670\(92\)85276-C](https://doi.org/10.1016/0003-2670(92)85276-C)
36. Jäschke A et al (2017) Hydroxyquinoline-Calix[4]arene-Conjugates as Ligands for Polynuclear Lanthanide Complexes: Preparation, Characterization, and Properties of a Dinuclear Eu(III) complex. *Eur J Inorg Chem* 2017:894–901. <https://doi.org/10.1002/ejic.201601326>
37. Kersting B, Lehmann U (2009) Chemistry of Metalated Container Molecules. *Adv Inorg Chem* 61:407–470. [https://doi.org/10.1016/S0898-8838\(09\)00207-4](https://doi.org/10.1016/S0898-8838(09)00207-4)