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Development of ^{115}Cd/^{115m}In Generator for Industrial and Environmental Applications

Fernanda C. F. Camargo*[a], Amenônia M. F. Pinto[a], Rubens M. Moreira[a]

[a]Nuclear Technology Development Center, Brazilian Commission for Nuclear Energy, Belo Horizonte, Brazil
Presidente Antônio Carlos Avenue, 6627, Belo Horizonte -MG, Brazil
fcfc@cdtn.br

Indium isotopes, ^{111}In, ^{113}In and ^{115}In are widely used as radiotracers in industrial and environmental applications. ^{113m}In generators can be found in the international market. However they are manufactured by only a few companies worldwide, they are rated at rather high prices and not always they are available for sale (they are frequently manufactured only upon request). Hence it is of interest to produce the equipment in the country in which it will be used, especially if the parent nuclide can be also produced there. In Brazil, for instance, the ideal situation would be to produce a ^{115}Cd/^{115m}In generator, whose precursor is ^{114}Cd. The irradiation conditions of the isotopically enriched ^{114}CdO target were defined according with the neutron flux provided the by a IPR-R1 TRIGA reactor and the nuclear properties of the target. Column experiments were performed with the ^{115}Cd/^{115m}In pair. The parent and daughter nuclides were separated percolating the eluate containing the chemical species Cd^{2+} and In^{3+} through two ion exchange resins, Ag11A8 and Dowex 1x8. 1.0 mol/L HCl and 2 mol/L HCl + 0.1 mol/L NH_4Cl solutions were tested as the eluent. Analyses were accomplished by gamma spectrometry to determine the presence of ^{115}Cd and ^{115m}In nuclides in the eluted fractions. Further tests using non-enriched and inactive CdO were performed to confirm the results. The amount of eluted Cd^{2+} and In^{3+} was determined by ICP-AES. Tests using resin Ag11A8 and 1.0 mol/L HCl eluent solution resulted in 100 % adsorption of the Cd^{2+} and nearly 50 % elution of In^{3+}, corresponding to the best conditions for elution.

1. Introduction

Radioisotopes have been applied in diverse areas such as medicine, industry, agriculture, environment and scientific research (Sood, 2003). Artificial radionuclides are mainly produced in nuclear reactors and particle accelerators by exposing certain target materials to a suitable neutron flux or to charged particles (International Atomic Energy Agency, 2003, 2009). An alternative for producing radionuclides that may be of interesting in several applications is provided by the radionuclide generators (Bjornstad, 2006).

There are many useful pairs of isotopes that can be used in radionuclide generators. However, only a small number of the already developed or proposed generator systems have been used in practice due to the scarce availability of the parent radionuclides and/or the complexity of the separation techniques (International Atomic Energy Agency, 2011; Lambrecht, 1983). Currently, there are a few generators that are useful for experiments with tracers in locations far away from the production site. Examples are the ^{62}Zn/^{62}Cu, ^{68}Ge/^{68}Ga, ^{82}Sr/^{82}Rb, ^{99}Mo/^{99m}Tc, ^{113}Sn/^{113m}In and ^{137}Cs/^{137m}Ba generators (International Atomic Energy Agency, 2010). The radionuclides ^{62}Cu, ^{68}Ga, ^{82}Rb are positron emitters used in positron emission tomography (PET) whereas ^{99m}Tc, ^{113m}In and ^{137m}Ba are gamma emitters, useful both in nuclear medicine and in industry (International Atomic Energy Agency, 2004). The ^{99}Mo/^{99m}Tc generator is the most widely used, even in industrial and environmental applications, but its supply has been recently threatened by paralysis a few aged reactors which produce ^{99}Mo. One important alternative is the ^{113}Sn/^{113m}In pair. However, many research reactors do not have a sufficiently intense neutron flux to produce the ^{113}Sn parent. A way out of this problem would be the use of the ^{115}Cd/^{115m}In system. The parent ^{115}Cd can be produced by irradiation of the most abundant isotope of cadmium in a research reactor of relatively low neutron flux. In order to booster the yield the target should consist of isotopically enriched ^{114}Cd which is

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commercially available in the international market at prices far below those of ^{113}Sn. Although the half-life of ^{115}Cd (53.5 h) is much shorter than that of ^{113}Sn (115.1 d), it can be produced even in small research reactors, as small as the IPR-R1 TRIGA (100 kW) reactor at the authors´ Institute (CDTN/CNEN) with a flux of 6.6 x10^{11} n/cm^2.s. What is lost in the time of life of the daughter nuclide is compensated by the advantage of doing without a high-power reactor.

The nuclide ^{114}Cd can be used as a precursor to ^{115}Cd because it has a high cross section for the ^{114}Cd(n,γ)^{115}Cd reaction under thermal neutron irradiation. The ^{115}Cd parent decays producing ^{115m}In (4.486 h), which emits a beta particle with 840 keV and a monoenergetic gamma ray with 336 keV via isomeric transition. Thus, ^{115m}In is perfectly apt for applications in processes with duration of the order of hours (Yagi et al., 1982).

The present work aims at the study of the conditions of production, separation and decay of the parent/daughter nuclide pair in order to build a ^{115}Cd/^{115m}In generator. This generator is intended to be used in the study or measurement of industrial and environmental processes in a near future, as an initial stage for possible future applications in medicine.

The separation of the parent/daughter nuclide pair made use of the ion exchange behavior displayed in earlier experiments. Kraus and Nelson (1956) performed an extensive search of the ion exchange behavior of metals aiming at the separation of fission products. Other studies of systematic separations by anion exchange were presented by Saito (1984). Several studies were also published evaluating the behavior of cadmium ion exchange using amphoteric and anionic resins (Samczński and Dybczyński, 1997, 2002) and evaluating ^{115}Cd/^{115m}In generators systems (Ehrhardt et al., 1983).

2. Experimental

2.1 Materials and reagents

A mass of about 11.5 mg of 99.10 % enriched ^{114}CdO (Euriso – Top) was irradiated in the IPR-R1 TRIGA reactor at CDTN for 8 hours at a neutron flux of 6.6 x 10^{11} n/cm^2.s to obtain the ^{115}Cd parent. The irradiation conditions were defined according to the needed activity, the nuclear characteristics of the ^{114}Cd target, the neutron flux provided by the reactor and the radiological protection conditions enforced at CDTN.

A high purity germanium detector (HPGe), model GC5019, with 50 % relative efficiency was used to measure the irradiation products as well as the eluates obtained from the experiments with irradiated ^{114}CdO. The gamma spectra were obtained using the Genie – 2000 Basic Spectroscopy (Standalone) V1.4 and Origin Pro 8 softwares.

Elution tests were also performed using non enriched CdO as well as In_2O_3 in order to ascertain the purity of the eluates. The Cd^{2+} and In^{3+} concentrations were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

The performance of two different stationary phases was evaluated, the styrene-*co*-divynilbenzene resins Ag11A8 (50-100 mesh) and Dowex1x8 (20-50 mesh). These resins had been tested in previous work and showed a potential for radionuclide separation. The mobile phase and eluent were defined taking into account the findings of other studies. The ion exchange separations were performed in open columns packed with the resins.

All reagents used in the present experiments were pure grade.

2.2 Procedure

The ion exchange bed was initially washed in sequence with 1.0 mol/L NaOH, water, 1.0 mol/L HCl, and then again with water. The oxides were dissolved in hot concentrated HCl. After drying the solution 2.0 mol/L HCl was added and the solution was once again taken to dryness. This procedure was repeated twice. The dry solid residue was taken with 2.0 mol/L HCl. These solutions were injected at the top of the column. Then the bed was eluted and samples were collected for analysis.

3. Results and discussions

The irradiated ^{114}CdO targets exhibited an average activity of 2.5 MBq. The elutions were performed only 1 week after the irradiation of the ^{114}CdO targets to fit their activities to the detector sensitivity. Figure 1 shows a gamma spectrum of the irradiated ^{114}CdO samples before separation. As expected, only the energies corresponding to the parent ^{115}Cd (261 keV, 492.4 keV and 527 keV) and daughter ^{115m}In (336.6 keV) in the energy range of interest, avowing the purity of the target material and eliminating any possibility of spectral interferences or production of other radioisotopes.

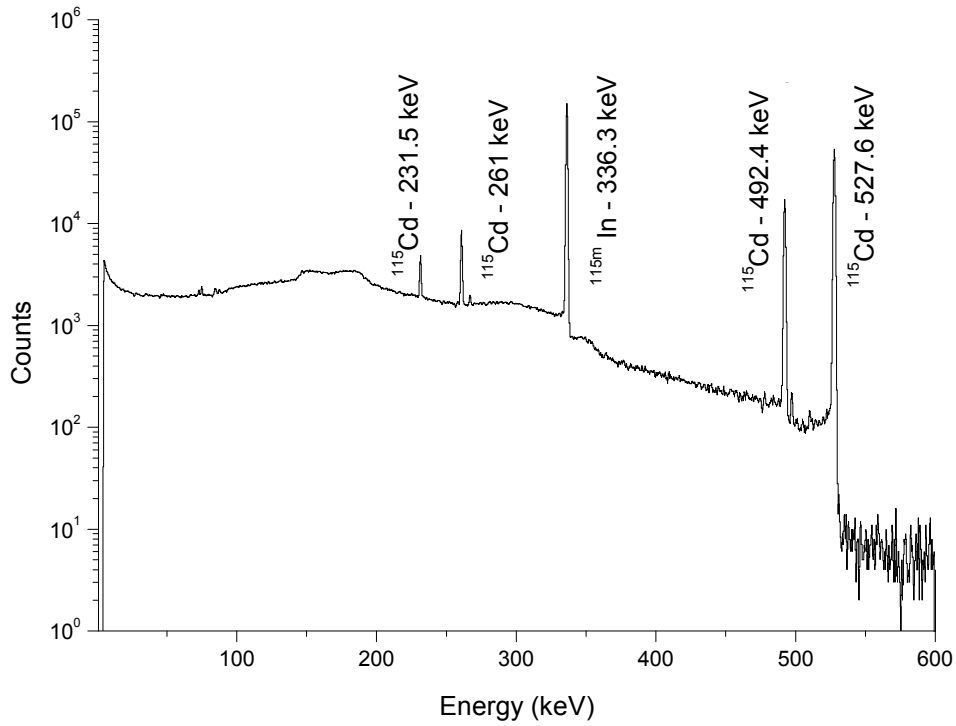

Figure 1: Gamma spectrum obtained with a HPGe detector of a ^{114}CdO target irradiated in the IPR-R1 TRIGA reactor, before separation of ^{115}Cd and ^{115m}In

Figures 2 and 3 show the elution curves obtained with the two elution conditions, each one replicated in different types of resins. The activity of the eluates was measured with the ^{115m}In radionuclide.

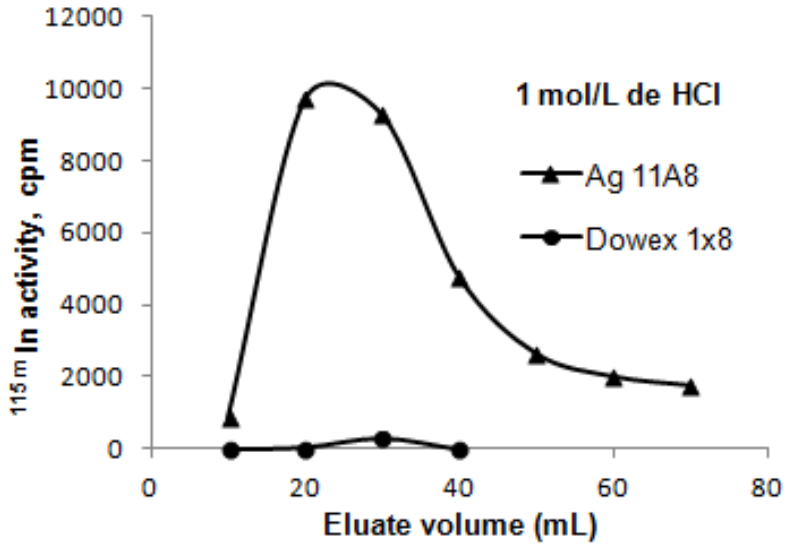

Figure 2: Elution curve of ^{115m}In from a generator system, for two different resins washed with 1.0 mol/L HCl solution

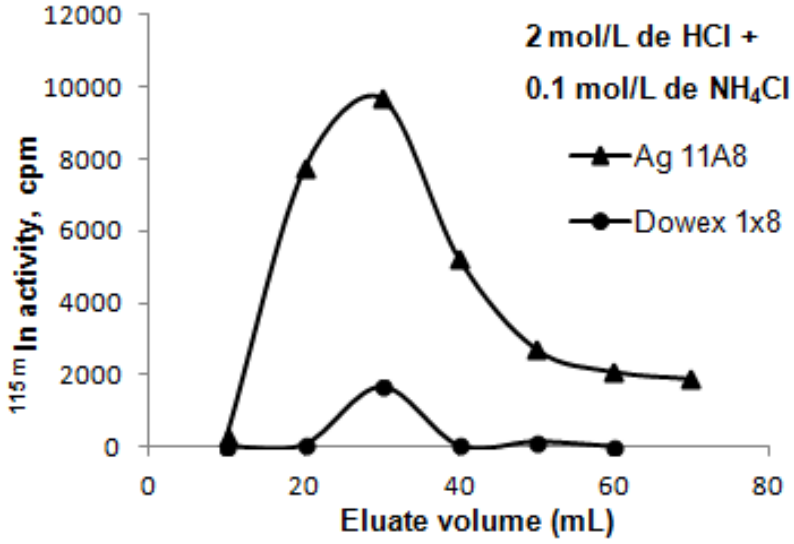

Figure 3: Elution curve of ^{115m}In from a generator system, for two different resins washed with 2.0 mol/L HCl + 0.1 mol/L NH_4Cl solution

As noted in Figure 2 and Figure 3, in the experiments performed with the Dowex1x8 resin only a small amount of ^{115m}In is eluted from the column as compared the same elution conditions of the Ag11A8 resin. The best results were obtained in experiments employing the Ag11A8 resin since it retained 100 % of the ^{115}Cd isotope and eluted a much larger amount of ^{115m}In in comparison with Dowex 1x8.

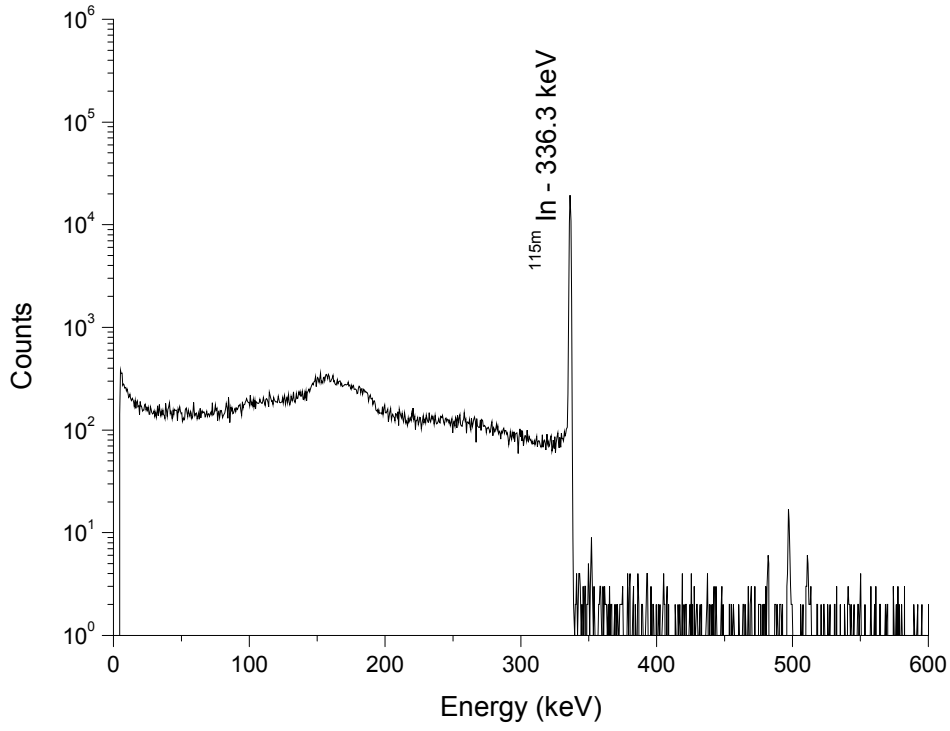

Figure 4: Gamma spectrum of a ^{114}CdO target irradiated in the IPR-R1 TRIGA reactor after separation of ^{115}Cd and ^{115m}In, obtained with a HPGe detector

The cadmium retention in the resins can be explained by the fact that aqueous solutions of cadmium halides, CdX_2, where X = Cl or Br, or I, exhibit complex equilibrium involving the $CdX_n^{(2-n)}$ configuration. Examples are the CdX^+, CdX_2, $[CdX_3]^-$ and $[CdX_4]^{2-}$ complexes. In hydrochloric acid solutions over 0.5 mol/L HCl there is a predominance of $[CdCl4]^{2-}$ complexes. Indium in acidic solutions containing chloride ions form the $InCl_2^+$, $InCl_2^+$, $InCl_3^0$ and $InCl_4^-$ species. The $InCl_4^-$ species is relatively unstable, exhibiting stability only in very concentrated HCl solutions (about 8 mol/L) (Wood and Samson, 2006). $[InCl_4]^-$, $[InCl_5]^{2-}$ and $[InCl_6]^{3-}$ species can also occur in hydrochloric acid solutions. Furthermore, in aqueous solution indium salts become hydrolyzed and in acid solutions In^{3+} is coordinated with six water molecules (Tuck, 1983), hence it is no longer adsorbed by the resin.

Figure 4 shows a gamma spectrum obtained from the second eluted fraction of the same experiment shown in Figure 2. It can be seen that the radioisotope ^{115}Cd did not show up in this fraction, only the daughter nuclide ^{115m}In (336.27 keV) is present. In all experiments the ^{115m}In (336.27 keV) peak was observed in the second eluted fractions.

Experiments using not enriched and non-irradiated CdO and an indium oxide, In_2O_3, to simulate the presence of ^{115m}In were performed in the same manner as the experiments with irradiated ^{114}CdO. Figure 5 shows an elution curve of In^{3+} in the Ag11A8 resin washed with a 1.0 mol/L of HCl solution. The best results were obtained in experiments employing this resin since it retained 100 % of cadmium and eluted about 50 % of indium.

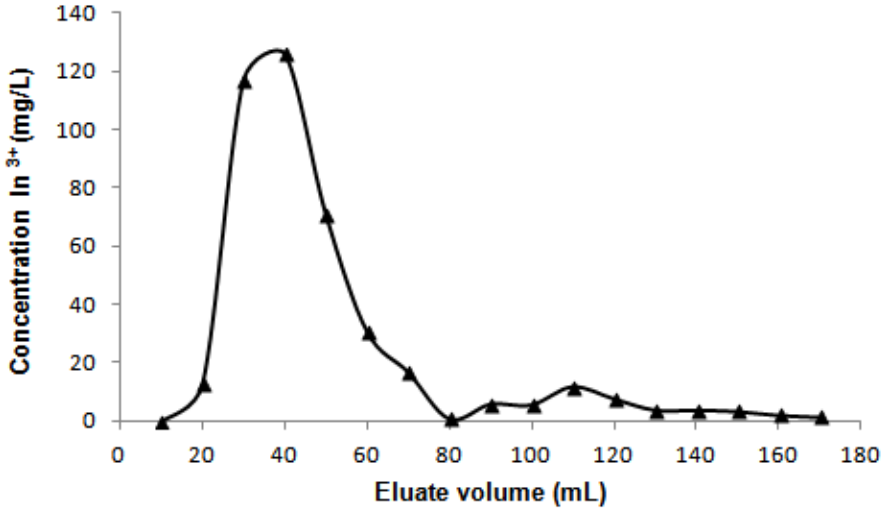

Figure 5: Elution curve of In^{3+} from a generator system with Ag11A8 resin washed with 1.0 mol/L HCl solution

4. Conclusion

This study aimed to develop a ^{115}Cd/^{115m}In generator for industrial and environmental applications. The radionuclide generator system proposed is based on the radiochemical separation of the ^{115}Cd and ^{115m}In nuclides by ion exchange. ^{115}Cd was retained on a strongly basic ion exchange resin and it decays to the daughter isotope ^{115m}in, which could be eluted from the column by an appropriate solution.

A series of experiments were performed, two resins were tested and the best conditions for obtaining ^{115m}In occurred in elutions using the Ag11A8 resin and 1.0 mol/L HCl solution. These conditions sands out due to complete retention of cadmium and elution of a significant amount of indium. The experiments with inactive CdO and In_2O_3 have shown that about 50 % of the indium added to the system is eluted.

Acknowledgments

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