Radium-228 as a Target for Production of Thorium-229 in a Nuclear Reactor

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Radium-228 as a Target for Production of Thorium-229 in a Nuclear Reactor

Master’s Project

Burnham, Chelsea A.
11/7/2013
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Abstract

The goal of this project is to research production methods for thorium-229, which is in demand for medical treatments, namely through the neutron activation of a radium-228 target. At ORNL, there are several hundred quality-analysis (QA) samples in storage from actinium-225 production during 1997-2007 which contain minute amounts of radium-228. 228Ra is the first alpha-decay daughter of thorium-232, which is the main constituent of the thorium-229 stock currently used for 225Ac production. Every 60 days, a mass containing both Ac and Ra is separated from the 229Th stock and then further separated using column chromatography to separate Ac from Ra. Since 225Ra decays to 225Ac with half-life of 14.8 days, a bi-weekly run of the Ra pool separated from the Ac product is also processed to provide smaller batches of 225Ac. The quality analysis samples of the Ra pool taken during processing are typically 5 µL from 1 mL and often contain 228Ra. These samples are combined and purified for 228Ra target production.

To observe isotope production cross sections, the target is irradiated for a short amount of time at the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory (ORNL). Due to the small amount of 228Ra collected, the main goal of the neutron activation was not primarily 229Th production, but to observe any characteristic gamma rays emitted from the intermediate isotopes 229Ra and 229Ac, since much about these isotopes are unknown.

In addition to observing the \( ^{228}\text{Ra} [n,\gamma]^{229}\text{Ra}(^{t_{1/2} = 4.0 \text{ min}, \beta^-}^{229}\text{Ac}(^{t_{1/2} = 62.7 \text{ min}, \beta^-}^{229}\text{Th}) \) reaction upon the irradiation of a target, the second step of this research was identifying key contaminants present in the thorium stock, such as americium-241, that may interfere with future large-scale target production. The QA samples taken from the separation of the Ac/Ra from the 229Th stock contain a noticeable amount of 241Am. Confirming this isotope and locating its source is crucial in this isotope research because there does not seem to be a logical parent isotope found in the thorium stock. Alpha and gamma analysis, as well as mass spectrometry are used to identify the 241Am.
Introduction

Alpha-emitting radioisotopes have become of interest for short-range site specific therapy for cancers such as acute myeloid leukemia, in particular bismuth-213.2 These particles are able to deliver high LET alpha particles with a much shorter range at targeted tumors, protecting surrounding healthy tissue from being damaged. $^{213}\text{Bi}$ emits an 8 MeV alpha particle that can penetrate 6 to 10 surrounding cell layers, including the targeted tumor cells. Both $^{213}\text{Bi}$ and its parent, $^{225}\text{Ac}$, have been shown in preclinical studies to be successful in the treatment of cancer systems and targeted radiotherapy.2

$^{225}\text{Ac}$ is the daughter produced in the decay of $^{229}\text{Th}$, and as a result, one method of obtaining $^{225}\text{Ac}$ is to glean it from a stock of $^{229}\text{Th}$. Uranium-233 has been the source of the current stock of $^{229}\text{Th}$. Originally, the $^{233}\text{U}$ used for the thorium stock was produced for the U.S. molten salt breeder reactor research program. Since abandoning the program, $^{233}\text{U}$ was stored at ORNL along with the waste material from the original $^{233}\text{U}$ production campaigns that spanned ~35 years. $^{233}\text{U}$ is part of the neptunium-237 series. Neptunium, the first transuranic element, does not occur in nature but is commonly found as a by-product in spent fuel rods of a nuclear reactor upon the capture of four neutrons by $^{233}\text{U}$ and subsequent $\beta^-$ decay ($t_{1/2}$=6.75 d) to $^{237}\text{Np}$.

The U.S. molten salt breeder reactor research program was developed as an effort to generate low-cost power under more efficient circumstances. Molten salt reactors are able to function at higher temperatures than water-cooled reactors, resulting in higher thermodynamic efficiency, while maintaining a low pressure. Sustaining a system pressure near atmospheric pressure reduces the amount of stress and corrosion the system undergoes during operation thus improving safety aspects of the system, as well. Fluid fuel in the form of UF$_4$ and ThF$_4$ is dissolved in fluorides of beryllium and lithium and circulated through the reactor core and moderated by graphite.4 $^{233}\text{U}$, which has similar fission characteristics to the more commonly recognized $^{235}\text{U}$, was produced during the reactor operation from 1970-1976. When natural
Thorium is irradiated in a reactor, the once non-fissile material is converted to one that is fissile. Natural thorium is essentially 100% $^{232}\text{Th}$, and when it is excited during the irradiation process, it is transformed into fissile material which quickly decays, forming $^{233}\text{U}$. $^{233}\text{U}$ is produced by the reaction $^{232}\text{Th} (n,\gamma) ^{233}\text{Th} (\beta^{-}, t_{1/2}=22.3 \text{ min}) ^{233}\text{Pa} (\beta^{-}, t_{1/2}=27 \text{ d}) ^{233}\text{U}$. Uranium-233 then decays to $^{229}\text{Th}$, shown in Figure 1, which has thus far been the only viable source of the isotope.

![Figure 1 Decay chain of uranium-233](image-url)

From 1995-1996 efforts were made to separate and purify $\approx 90$ mCi of $^{229}\text{Th}$ from the stored waste, and since then an additional $\approx 60$ mCi has been recovered from other stored $^{233}\text{U}$ oxides. The combined $^{229}\text{Th}$ stock has been the source for the $^{213}\text{Bi}$ used for medical treatments currently being conducted. $^{229}\text{Th}$ decays to $^{225}\text{Ac}$ by way of $^{225}\text{Ra} (t_{1/2}=15 \text{ d})$. Once this $^{225}\text{Ac}$ is removed from the thorium stock using chemical separation it can be loaded in a generator system. This generator system will contain the $^{213}\text{Bi}$ decay daughter produced from actinium which is subsequently delivered to the patient. During this production process, quality analysis
(QA) samples are routinely taken, typically 5 µL from 1 mL, and then stored. Since the beginning of the actinium project in 1997, several hundred QA samples have accumulated. As a part of quality control, after one year of decay, these QA are routinely re-analyzed by both gamma-ray spectroscopy and mass spectrometry to measure any leaking of $^{229}$Th and metal contamination into the purified Ac/Ra during chemical processing. After one-year of decay, the γ-ray spectrum of the $^{225}$Ac QA samples typically show minute amounts of $^{229}$Th, but some show somewhat larger amounts of $^{228}$Th ($t_{1/2}=1.8$ y). The $^{228}$Th has been attributed to presence of $^{228}$Ra($t_{1/2}=5.75$ y) in the Ac samples. Note that $^{228}$Ra is the first alpha decay product of $^{232}$Th ($t_{1/2}=1.405 \times 10^{10}$ y), which accounts for 99.5 mass % of the thorium stock solution. Miniscule amounts of $^{228}$Ra are extracted, along with other Ra/Ac daughters during the chemical processing of $^{229}$Th which is performed every 60 days. Consistently during the routine analysis of the $^{225}$Ac QA sample, in addition to the gamma rays from $^{228}$Ra/$^{228}$Th, there has also been a significant signal at 60 keV, whose origin remains unknown. This signal, in relation to the entire sample spectrum, can be seen highlighted in red in Figure 2, and Figure 3 also shows a detailed view of this signal. Due to the proximity of this gamma ray to 59.5 keV, it was thought perhaps this gamma ray could belong to americium-241 ($t_{1/2}=432$ y). The first part of this research focused on proving or disproving if the 60 keV gamma ray was indeed originating from $^{241}$Am. If americium was present as impurity in the $^{229}$Th stock, it should have been completely eliminated in the first few extractions of Ra/Ac from Th stock as the chemistry of Am$^{3+}$ and Ac$^{3+}$ is very similar. Therefore, the presence of Am in all Ac QA samples can only be possible if Am is generated through decay of an long-lived radioisotope who’s chemistry is similar to Th. $^{241}$Am is the beta decay daughter of plutonium-241 ($t_{1/2}=14.35$ y), and chemistry of Pu$^{4+}$ very much resembles that of Th$^{4+}$. In this work, the likelihood of this contaminant is investigated, and its presence or absence is confirmed using gamma spectroscopy and alpha spectroscopy, as well as a mass analysis to confirm the $^{241}$Pu parent.
The second part of this report describes the effort toward concentrating and purifying the miniscule amounts of $^{228}\text{Ra}$, which were present in the $^{225}\text{Ac}$ and $^{225}\text{Ra}$ QA samples. $^{228}\text{Ra}$ is considered to be a valuable target material for production of $^{229}\text{Th}$ in a nuclear reactor through the following nuclear reaction.

$$^{228}\text{Ra}([n,\gamma])^{229}\text{Ra} (\beta^-, t_{1/2}=4.0 \text{ min})^{229}\text{Ac} (\beta^-, t_{1/2}=1.05 \text{ h})^{229}\text{Th}$$
It is anticipated that the demand for treatment of cancer with $^{213}$Bi and $^{225}$Ac will soon outgrow the $^{229}$Th stock available at ORNL, sparking the investigation of other sources for high purity $^{229}$Th. The above reaction, involving only one neutron capture, is expected to produce a higher $^{229}$Th yield and smaller amounts of radiocontaminants than $^{226}$Ra targets ($t_{1/2}=1600$ y) which involves three neutron captures followed by three $\beta^-$ decay. This path is indicated by the red arrows in Figure 4. Of course, if this method of $^{229}$Th production proves to be successful the issue of $^{228}$Ra availability will need to be addressed.

![Figure 4](image)

**Figure 4** $^{228}$Ra captures a neutron and beta decays twice, yielding $^{229}$Th (path shown in red)

As pointed out, $^{228}$Ra is the first alpha decay product of $^{232}$Th ($t_{1/2}=1.405 \times 10^{10}$ y), which accounts for 99.5 mass % of the ORNL $^{229}$Th stock. During the Th/Ac processing campaigns, performed every 60 days, 0.30 μCi (1.1 ng) of $^{228}$Ra is also extracted, along with other Ra/Ac daughters. The growth of the $^{228}$Ra daughter as a function of time can be seen in Figure 5. As noted earlier, the QA samples of the Th/Ra/Ac processing all contain $^{228}$Ra. The second part of this research describes extraction and purification of $^{228}$Ra from the QA. The purified $^{228}$Ra then was used to prepare several small targets for irradiations at the neutron activation facility, which is a part of the ORNL High Flux Isotope Reactor (HFIR). The goal was to synthesis $^{229}$Ra ($t_{1/2}=4.02$ m) and its beta decay daughter $^{229}$Ac ($t_{1/2}=62.7$ m), as shown in the above reaction.
Very little is known about these nuclides; no gamma-rays are reported for $^{229}$Ra and the absolute intensities of the gamma rays following the decay of $^{229}$Ac are also presently unknown.

![Figure 5](image.png)

**Figure 5** $^{228}$Ra daughter growth from the $^{232}$Th parent

To verify the yield of $^{229}$Th from the neutron bombardment of $^{228}$Ra target, a larger amount of $^{228}$Ra was extracted from several kg of $^{232}$Th to produce a target. The extraction and purification of $^{228}$Ra from $^{232}$Th was conducted by another student and this target is currently, as of October 2013, being irradiated in HFIR for one full cycle (24 days).

**Experimental Method**

**Chemistry**

In order to perform the chemical steps for the separation of $^{228}$Ra/$^{228}$Ac from thorium and other large amounts of radiocontaminants, high-purity HNO$_3$ as well as HCl are used in conjunction with exchange resins. These resins include the anion exchange resin MP1 (200-400 mesh; Cl$^-$ form) and the MP50 (100-200 mesh; Na$^+$ form) and AG50 (200-400 mesh; Na$^+$ form)
cation exchange resins. The MP1 resin was converted to nitrate form for one of the columns by rinsing it with several bed volumes (BV) of 8M HNO₃ to remove all of the Cl⁻ ions present. The reagent H₂O₂ is used for further clean-up of the sample. Disposable Bio-Rad polypropylene columns pre-fitted with a frit are used.

The following columns are constructed to conduct chemical separation on the samples. The clean-up done on the QA samples for ²⁴¹Am observation used columns I and IV while columns I, II, III, and IV were all utilized in the clean-up for the target production since a higher purity was essential to obtain results from the irradiation. The procedures used for each experiment can be seen in Figures 6 and 7.

**Column I** A MP1 (200-400 mesh) column is built to remove any trace amounts of thorium that still remain in the QA samples.² After rinsing the poly-prep column with several milliliters of deionized water, a resin BV of 0.8 mL (1 mL BV for radium pool samples) is added to the column and sparged to remove any bubbles and prevent channeling in the resin bed. Once the resin bed has settled, a ball of glass wool is gently placed on the top of it. For this separation the resin must be converted to nitrate form; thus, it is conditioned with two BV of 8M HNO₃ and subsequently eluted with several more BV of deionized water and stored until use.

**Column II** MP50 (100-200 mesh) resin is used as a reverse phase chromatographic system for further purification of QA samples.² A resin BV of 0.5 mL is used with HNO₃ to prepare highly purified samples of radium. The column is prepped in a similar method as Column I, this time using a lower acid concentration of 0.1 M. The MP50 column removes sodium and lead contaminants that are present in the sample.

**Column III** Another MP1 (200-400 mesh) column is prepared, this time using a BV of ~200 µL BV which is subsequently conditioned with 9M HCl. This column will remove any trace amounts of iron contained by the sample.²

**Column IV** Several AG50 resin columns (200-400 mesh) with BV of ~200 µL are used in the final steps of the sample purification. Using a column that has been washed with several BV of 0.12 M HNO₃, radium is separated from isotopes such as americium-241 and actinium-228.²
Figure 6 Clean-up procedure used to process $^{228}$Ra target material
Radioactivity Measurements

Gamma analysis

Gamma analysis of the material was performed using a calibrated High Purity Germanium (HPGe) detector in conjunction with a PC-based multi-channel analyzer. HPGe detectors deliver excellent resolution in radiation measurements for a large energy range. The detector efficiency with respect to photon energy is shown in Figure 8 and includes the efficiency at various shelf locations above the detector face. For the purpose of this low-activity experiment, a shelf 2 cm above the detector face was used for most measurements. Activity
calculations based on their respective energies are performed using data provided by the National Institute of Standard and Technology (NIST) and Equation 1 below.

\[
\text{Activity (\(\mu\text{Ci}\))} = \frac{\text{Total Counts}}{\text{Time (s)}} \left[ \text{efficiency} \times \frac{\% \text{ Gamma Intensity}}{100} \times \frac{3.7 \times 10^4 \text{decay}}{1 \mu\text{Ci}} \right]^{-1}
\]

Equation 1 Calculates the activity of a specified isotope based on the total counts

The key gamma rays observed in this project are listed in Table 1. For observation of \(^{241}\text{Am}\), the distinct gamma ray of 59.5 keV was used based on the relatively high intensity and energy resolution. \(^{228}\text{Ra}\) does not emit any significant gamma rays; therefore the gamma rays of its decay daughter, \(^{228}\text{Ac}\), are used as a tracer for this isotope. Since the efficiency of the detector decreases significantly for higher energies, the average activity is calculated based upon the signal from the 338.4 keV, 911.1 keV, and 968.9 keV gamma energies. These were chosen because they are due solely to \(^{228}\text{Ac}^{228}\text{Ra}\) in the sample.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Energy (gamma) keV</th>
<th>Intensity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ra-225</td>
<td>40.1</td>
<td>39.30%</td>
</tr>
<tr>
<td><strong>Am-241</strong></td>
<td>59.5</td>
<td>35.90%</td>
</tr>
<tr>
<td>Th-229</td>
<td>193.6</td>
<td>5.89%</td>
</tr>
<tr>
<td>Th-229</td>
<td>210.9</td>
<td>4.00%</td>
</tr>
<tr>
<td>Th-229/Fr-221</td>
<td>218.0</td>
<td>13.40%</td>
</tr>
<tr>
<td>Ra-228/Pb-212</td>
<td>238.6</td>
<td>64.90%</td>
</tr>
<tr>
<td><strong>Ra-228/Ac-228</strong></td>
<td>338.4</td>
<td>12.00%</td>
</tr>
<tr>
<td>Ac-225/Bi-213</td>
<td>440.4</td>
<td>27.50%</td>
</tr>
<tr>
<td>Ra-228/Bi-212</td>
<td>583.1</td>
<td>46.00%</td>
</tr>
<tr>
<td><strong>Ra-228/Ac-228</strong></td>
<td>911.1</td>
<td>29.00%</td>
</tr>
</tbody>
</table>
Figure 8 Efficiency curve for one of the HPGe detectors used for gamma analysis of the sample

Alpha Analysis
Alpha spectroscopy is performed using a silicon detector and analyzed using a PC-based multichannel analyzer. The ORTEC alpha spectrometer used has a detector efficiency $>25\%$ for a detector source spacing $<10$ mm.$^5$ This detector includes a low-background sample chamber where the sample is placed in a vacuum during the time of the data collection. The system is quickly calibrated using the spectrometer pulsar that delivers a signal at distinct energies. From these known signals, the signal produced by the samples can be confirmed. The alpha energies emitted by $^{241}\text{Am}$ are shown in Figure 9. An analysis is done to observe if the 5.49 MeV alpha particles emitted by $^{241}\text{Am}$ are present, and is then compared to a similar analysis of a standard. Since this analysis was performed to solely confirm its presence, the calculation of the activity based upon this measurement was omitted to save time.

![Figure 9 Alpha decay of $^{241}\text{Am}$](image)

<table>
<thead>
<tr>
<th>$E_\alpha$/MeV</th>
<th>$E_\gamma$/keV</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_1$: 5.389</td>
<td>$\gamma_1$: 26.3</td>
</tr>
<tr>
<td>$\alpha_2$: 5.443</td>
<td>$\gamma_2$: 33.2</td>
</tr>
<tr>
<td>$\alpha_3$: 5.486</td>
<td>$\gamma_3$: 43.5</td>
</tr>
<tr>
<td>$\alpha_4$: 5.513</td>
<td>$\gamma_4$: 59.5</td>
</tr>
<tr>
<td>$\alpha_5$: 5.545</td>
<td>$\gamma_5$: 99.0</td>
</tr>
<tr>
<td>$\gamma_6$: 103.0</td>
<td></td>
</tr>
<tr>
<td>$\gamma_7$: 158.5</td>
<td></td>
</tr>
</tbody>
</table>

**Methodology**

The two different $^{228}\text{Ra}$ sample sources were purified based on the chemical properties of the contaminants they contained. The consolidated samples were separated in two groups: those coming from routine QA samples and those samples taken from the radium pool. The QA samples were used in experiments confirming the presence of $^{241}\text{Am}$ contaminant and samples
taken from the radium pool samples were purified for target production since they contained more significant amounts of $^{228}$Ra.

**Quality Analysis Samples**

Quality analysis samples taken during the $^{225}$Ac campaign processed from 1997 to 2007 were consolidated and cleaned for further isotope research. It was crucial that the samples be at least 3 months old to ensure that any traces of $^{225}$Ac had decayed away to a negligible amount. Like any impurity, the presence of this isotope in the sample would produce unnecessary radiocontaminants and possibly mask the isotopes of interest during the neutron activation process.

Approximately 300 sample vials were collected and 25 were consolidated at a time. The 25 vials were arranged in five rows and five columns. A pipette was used to place 1 mL 1.2 M HNO$_3$ in each back row vial. The solution was transferred by pipette to the next row until all were cascade rinsed and collected in a single sample bottle. The vials were rinsed once more with 1 mL 8 M HNO$_3$ to ensure that all radioactive material had been removed. This was repeated $\sim$12 times and the consolidated samples were placed in glass bottles labeled QA #1-$\#6$ then evaporated to dryness. Using high purity HNO$_3$, the contents of the bottles were combined in bottle QA#4, which contained the most activity. The sample bottle was counted using an HPGe detector to determine its constituents. Since these samples contained only minute amounts of $^{228}$Ra, they were excluded from the target production and cleaned-up for further analysis of its components, $^{241}$Am being of main concern.

Column I is used for primary clean-up of the sample. The load solution for this column, bottle QA #4, contained 4.38±0.13µCi of $^{229}$Th, so this column was used to separate that isotope from the rest of the sample. The $^{229}$Th is recovered in the elution fraction by running 4x1 mL 0.12 M HNO$_3$ through the column. The load fraction from Column I is purified further using Column IV. The load solution (0.12 M HNO$_3$) is placed in the column. Two washes of 1.2 M HNO$_3$ remove the $^{228}$Ra from the column and are collected. After this is done, gamma ray analysis is performed using an HPGe detector and compared to an americium standard. An alpha analysis is done to confirm once more that the alpha energy resembles that of the Am standard. Finally,
a mass analysis was performed on a sample from the thorium stock to confirm the possible sources of the americium impurity. This analysis gives a spectrum of all the masses present in the sample. While it is unable to identify the sources of the masses, it can be a useful tool in solving this kind of puzzle.

**Radium Pool Samples**

The QA samples taken from the radium pool were consolidated using the cascade rinsing technique described above, this time with 8M HNO3. Approximately 100 sample vials were consolidated and a gamma analysis was performed. An hour count determined that along with the $^{228}$Ra, the samples included the radiocontaminants $^{241}$Am (60 keV), $^{229}$Th/$^{221}$Fr (218 keV), and $^{225}$Ac/$^{213}$Bi (440 keV). The sample bottles also revealed to contain a yellowish residue when evaporated to dryness, most likely a result from the presence of iron or organic materials.

Column I x 2 is used to remove any trace amounts of thorium show in the gamma spectroscopy. The load samples were 16.5 mL 8 M HNO3 (2.01±0.12μCi $^{228}$Ra) for the first column and 12 mL 8 M HNO3 (2.54±0.14μCi $^{228}$Ra) for the second. The load was collected in two fractions, L1 and L2 for the first column and L3 and L4 for the second. The column was then eluted with 5 mL of deionized water. The $^{228}$Ra goes through the column with the highly concentrated acid, while the $^{229}$Th remains in the column until it is eluted. The load solutions are then evaporated to dryness and observed once more using an HPGe detector. In order to remove the visible organic material present in the load fractions, the bottles were rinsed with 6 drops of 8M HNO3 and H₂O₂ at a time and then the total rinse volume was evaporated to dryness.

Column II is used next to further purify the sample. In this column, the $^{228}$Ra is removed in the strip fraction. The load solution is made up of the sample dissolved in 0.1M HNO3. It is then washed with 5 mL 2 M HNO3 and stripped in two fractions, 3 mL 8 M HNO3 into S1 and 2 mL water into S2. After this column was run, all of the combined and purified radium was stored in a single bottle. Six drops of 8 M HNO₃ and H₂O₂ were added once again to this bottle to remove any organic material and then evaporated to dryness. A 10-hour gamma
spectroscopy was done to observe any small amounts of radiocontaminants still present. The
gamma analysis can be seen in Table 2.

<table>
<thead>
<tr>
<th>Bottle ID</th>
<th>L4 (All Ra Combined) &quot;Dry&quot;</th>
<th>Lab 103</th>
<th>counted: 8/1/2011</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ra-225</td>
<td>214000</td>
<td>360000</td>
<td>5.94</td>
</tr>
<tr>
<td>Am-241</td>
<td>266000</td>
<td>360000</td>
<td>7.39</td>
</tr>
<tr>
<td>Th-229</td>
<td>0</td>
<td>360000</td>
<td>193</td>
</tr>
<tr>
<td>Th-229/Fr-221</td>
<td>3890000</td>
<td>360000</td>
<td>108.06</td>
</tr>
<tr>
<td>Ra-228/Pb-212</td>
<td>466000</td>
<td>360000</td>
<td>1.29</td>
</tr>
<tr>
<td>Ra-228/Ac-228</td>
<td>5480000</td>
<td>360000</td>
<td>15.22</td>
</tr>
<tr>
<td>Ac-225/Bi-213</td>
<td>4010000</td>
<td>360000</td>
<td>111.39</td>
</tr>
<tr>
<td>Ra-228/Bi-212</td>
<td>312000</td>
<td>360000</td>
<td>0.87</td>
</tr>
<tr>
<td>Ra-228/Ac-228</td>
<td>4630000</td>
<td>360000</td>
<td>12.86</td>
</tr>
<tr>
<td>Ra-228/Ac-228</td>
<td>2670000</td>
<td>360000</td>
<td>7.42</td>
</tr>
</tbody>
</table>

Column III is utilized to remove any iron present in the sample. A strong HCl solution
causes the Fe\(^{+3}\) to form negatively charged chloro-complexes. These ions are strongly retained
by anion-exchange resins, such as MP1. Furthermore, Ra and Ac show little or no retention by
the resin when using highly concentrated hydrochloric acid.\(^2\)

The final clean-up is performed using Column IVx2. Nitric acid is used, 0.12 M in the load
solution, and then washed with a higher molarity of 1.2 M. Under experimental conditions, a
molarity of 1.2 was found to be optimum for separating >90% radium from the actinium
sample.\(^2\) Because \(^{241}\)Am behaves similarly to actinium, the AG50 column was determined to be
the most efficient way to separate the contaminant from the radium while still maintaining a
high recovery rate of the \(^{228}\)Ra. Several small wash fractions are collected in separate bottles to
observe in which fraction the \(^{228}\)Ra is removed from the column. The elution profile is shown in
Figure 10. A 60-hour period from the time of separation must be observed before the sample
can be analyzed with a gamma detector since the $^{228}$Ac tracer isotope is separated with this column run.

![Figure 10 The elution profile of AG50 Column 1 in % of total activity](image)

The fractions containing $^{228}$Ra, washes 2-6, were combined for a 15-hour gamma spectroscopy which showed ~6.39±0.23μCi (23.43±0.82ng) $^{228}$Ra present in the sample along with 0.20±0.02μCi (104.28±5.79ng) $^{241}$Am. Since the mass of americium remaining in the sample was still quite significant, another AG50 column was used. The elution profile can be seen in Figure 11.
The behavior exhibited was not expected, and there was some breakthrough of $^{241}\text{Am}$ early on in the washes with a majority of the $^{228}\text{Ra}$. Washes 4, 7, and 8, that contain trace amounts of americium, are consolidated and put through one more AG50 column. The washes from this column run are re-added to the washes that contained no americium and evaporated to dryness. The amount of $^{228}\text{Ra}$ recovered from this clean-up was $\sim 3.11 \pm 0.16 \mu\text{Ci}$ (11.41±0.59ng) and the amount of americium left in the sample was reduced to $\sim 23.24 \pm 0.01 \text{nCi}$ (6.78±1.48ng).

**Target Production**

A total of three targets were fabricated for this project. The final purified sample was dissolved in 100 μL of high purity 0.12 M HNO$_3$ and a 10 μL sample was taken and placed in a quartz ampoule to be used in the first irradiation at HFIR. This ampoule is shown in Figure 12.
The second target was assembled for a second attempt to observe $^{229}$Ra by placing the remaining $^{228}$Ra sample of 2.31±0.14μCi (8.48±0.51ng) into a small plastic cup, seen in Figure 13, that is then placed in a plastic capsule designed to insert small amounts of material in a nuclear reactor. This container is also known as a “rabbit”, shown in Figure 14. To avoid problems faced in the first experiment the irradiation time was lowered to 60 seconds and plastic was used instead of quartz to avoid the enormous amount of radiocontaminants produced by the glass. Two cups were placed in the target, one with the radium sample and one containing the same amount of HNO$_3$ acid with zero activity.
Observing the longer lived intermediate isotope, $^{229}\text{Ac}$ ($t_{1/2}=1.05\ h$), was the objective of the third and final $^{228}\text{Ra}$ target. This isotope has no known discrete gamma energies and is typically identified through its daughter product. A quartz ampoule is used once more for this neutron activation experiment using the recovered radium from the second target, 1.83±0.12µCi (6.69±0.45ng). The irradiation time was increased to 120 minutes because of the longer half-life, but was also cooled for an hour before observation. To eliminate a majority of
the radioactivity present in the ampoule, the target was transported to a fume hood to perform chemistry eliminating these contaminants.

Once the third target arrived in the laboratory, the ampoule was immediately rinsed with high purity 8 M HNO₃ and deionized water, dried, and then broken in a clean bottle. 2 mL of 8 M HNO₃ were then added to the bottle to dissolve the radioactive material present. The solution was then separated from the broken glass using a pipette. The solution was evaporated and dissolved once more in HNO₃, this time with a lower molarity of 0.1M HNO₃, which is the most efficient for actinium separation in an AG50 column. The solution and a 1.5 mL wash of the glass bottle was loaded into the 200 μL BV column, prepared similarly to those used previously in the sample clean-up. Four 0.5 mL 1.2 M HNO₃ wash fractions were collected from the column and immediately counted to observe where the activity resided. Because of the high levels of contaminants that still remained in the sample, this process was done once more using only one 2mL 1.2 M HNO₃ wash and was counted for one hour, six times to observe any isotopes present in the sample. This chemical processing can be seen in Figure 15.

Neutron activation was done at the High Flux Isotope Reactor by sending the target, placed in a rabbit, through a tube directly in the reactor. Once positioned in the reactor, the rabbit was bombarded with neutrons at a thermal neutron flux of $2 \times 10^{15}$ n·s⁻¹·cm⁻². The irradiation time was short in order to minimize the contaminants produced by the quartz glass or plastic and other impurities of the sample. It was then immediately observed in an HPGe detector.
Results

Amercium-241 Sample Analysis

An alpha analysis was performed on the purified consolidated QA samples. The data collected for the sample and the standard was fit to a Gaussian distribution using MATLAB. The sample data points, shown in Figure 16, seem to be shifted to the left which is possibly due to attenuation through the plastic slide (thickness < 1 mm) used as a barrier between the open source sample and the detector face or from the attenuation through the mass of the contaminants that remain in the sample. To make up for this, a Gaussian curve was fit using the data points that demonstrated this behavior. The alpha spectroscopy of the sample is shown in Figure 17 and because most of the data points showed a Gaussian distribution, they were all weighted evenly. Using the fit line, the peak for both the sample and the standard are shown to occur in channel 641, which confirms that the two signals are most likely coming from the same source.
Figure 16 Alpha spectroscopy analysis of QA sample
To confirm the presence of americium in the sample, a gamma analysis comparison was performed for the sample and standard. The spectra are also fit to a Gaussian distribution using MATLAB. Like the alpha sample spectrum, the data points for the gamma sample are weighted so that line fit is created using the points exhibiting Gaussian behavior. The data points taken for the standard are all weighted equally. The spectrum of the sample, shown in Figure 18, shows a peak at channel 68.5, while the spectrum of the standard, shown in Figure 19, shows a peak occurring at channel 67.5. This 1.5% difference is noted, but with the data obtained from both the alpha and gamma spectra it is safe to assume the gamma peak is coming from the same source.
Figure 18 Gamma spectroscopy analysis of QA sample
Figure 19: Gamma spectroscopy analysis of $^{241}$Am standard

Though the analysis performed indeed confirm the presence of the americium contaminant in the quality analysis samples, the question still remains as to where the americium is coming from since its presence remains even after in depth clean-up efforts. The only explanation for the presence of americium after the sample clean-up is that there is an isotope present in the sample that remains after the wash then eventually decays to $^{241}$Am. The most plausible source for this isotope would be plutonium-241. However, a mass spectrometry performed on the thorium stock shows no traces of plutonium-241, as seen in the results shown in Figure 20. The mass spectroscopy does show distinct signals at 248 and 249 amu; however, those can be contributed to the dilution of the sample and are coming from $^{232}$Th$^{+16}$O and $^{232}$Th$^{+17}$(OH). Thus, the source of the americium-241 contaminant remains unknown.
**Radium-228 Target Irradiation**

A 10 μL 0.13±0.01μCi (0.46±.03ng) sample was taken from the consolidated ²²⁸Ra sample (100 μL 0.12 M HNO₃) and placed in a clean quartz ampoule to be put in a plastic rabbit for neutron activation. The first ²²⁸Ra target was irradiated in the HFIR August 23, 2012 at 13:41:59 for 120 seconds. The target was counted immediately following the irradiation ten times, each count time lasting five minutes. This gamma analysis was done using a heavily shielded HPGe detector located in a lab directly next to where the neutron activation takes place. After the ten-five minute counts were performed, the sample was counted ten more times, with an hour for each count. Observing the activity immediately following the irradiation was imperative in order to observe ²²⁹Ra (t₁/₂=4.0 m). ²²⁹Ra is formed when ²²⁸Ra absorbs a
neutron and then beta decays twice to the isotope of interest, $^{229}$Th. This isotope has no known gamma rays, so any information that could have been collected from the spectra would be valuable. The gamma ray spectroscopy results from this experiment are shown below in Figure 21 and Figure 22.

The main issue faced during the Target 1 irradiation was the activity created in the quartz ampoule. The yield of radioactive isotopes produced by interactions with $^{228}$Ra was minute in comparison to the activity produced from interactions in the quartz glass. The main contaminants produced by the glass are the short-lived aluminum-28, sodium-24, magnesium-27, and manganese-56. These all decay away within a few hours, but by that time the short-lived $^{229}$Ra has already decayed significantly from the sample.

![Figure 21 Radium-228 Target 1 taken 5 minutes after irradiation](image)
To avoid the radiocontaminants produced by quartz, a target was produced using a plastic cup in place of a quartz ampoule. A second blank target was irradiated at the same time to compare spectra between the two. On October 31, 2012 at 8:27:39 the targets were irradiated together for 60 seconds. During this irradiation time, the cup containing the $^{228}$Ra sample was opened due to the warping of the container caused by the heat produced during irradiation. Sodium-24 as well as manganese-56 impurities still remain abundant in both targets, which can be seen in Figure 23 and is still observable 50 minutes post-irradiation, seen in Figure 24. There were no recognizable differences between the $^{228}$Ra target spectrum and that of the blank cup.
Figure 23 Radium-228 Target 2 taken 5 minutes after irradiation
After unsuccessfully identifying any gamma rays possibly belonging from the short lived 229Ra, efforts were made to identify any characteristic gamma ray energies emitted from its daughter via beta decay, 229Ac. Chemistry was done to clean the target as much as possible before performing gamma spectroscopy on the irradiated sample. The 2 hours that was spent allowing the target to cool and subsequently transported to the lab for chemical purification allowed any 229Ac produced to undergo at least two half-lives. Figure 25 shows the a three hour spectrum of this sample which contained possible fission products but did not reveal any evidence of gamma ray energies emitted directly from the 229Ac.
Conclusion

Though $^{241}$Am was confirmed to be present using alpha and gamma spectroscopy, the source has yet to be identified. This contaminant could interfere with large-scale production, so a chemical separation process that completely removes the contaminant would be necessary in the future. The chemical process constructed for the potential removal of $^{228}$Ra from the $^{225}$Ac campaign process if the production of $^{229}$Th was successful with the irradiation of a $^{228}$Ra target. To collect more data for the research of $^{229}$Ra and $^{229}$Ac, a faster and more efficient chemical separation method will need to be developed to observe the isotopes before they quickly decay away. Also, due to time constraints, the clean-up immediately following the neutron activation had to be done in a laboratory where these chemical processes were authorized. If the laboratory located where the target is removed from the reactor is approved for these chemical processes, the likelihood of observing these short-lived isotopes would increase greatly. The unsuccessful attempts to observe these isotopes does not indicate that nothing was gained for
the experiment and knowing that certain methods are not effective will be useful in future efforts. In future work, a larger $^{228}$Ra target will be placed in HFIR to observe the production of $^{229}$Th. This target containing 181.3 μCi (0.7μg) of $^{228}$Ra will be irradiated for a full cycle (24 days) and chemical processing will begin starting in December 2013.

References


5 Soloist: Alpha Spectrometer Operating and Service Manual. EG&G ORTEC.


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