



Selective separation of radium and actinium from bulk thorium target material on strong acid cation exchange resin from sulfate media

Daniel R. McAlister^{a,b,*}, E. Philip Horwitz^{a,b}

^a PG Research Foundation, 1955 University Lane, Lisle, IL 60532, USA

^b Eichrom Technologies, LLC, 1955 University Lane, Lisle, IL 60532, USA



HIGHLIGHTS

- Efficient method for the separation of Ac and Ra from thorium target material.
- Complete method from target dissolution to purification.
- Eliminates need for evaporations.
- High purity Ac in high yield.

ARTICLE INFO

Keywords:

Actinium, ²²⁵Ac
²²⁷Ac

Ion exchange
Extraction chromatography
Nuclear medicine

ABSTRACT

This work presents a complete scheme for the selective separation of actinium and radium isotopes from bulk ²³²Th target material, in a process that may be applied in a separation scheme for the production of ²²⁵Ac by proton spallation on thorium. Thorium metal is dissolved in sulfuric acid with small amounts of HF. Actinium and radium are retained on cation exchange resin from the sulfate medium, while neutral and anionic thorium sulfate complexes are rejected. Following rinsing steps to remove residual thorium, actinium and radium are recovered from the cation exchange resin using 5 M HNO₃. Further separations of actinium via extraction chromatography with UTEVA and DGA resins yield actinium in > 92% yield, while providing additional decontamination from thorium and other spallation byproducts. The radium fraction can be further processed following ingrowth of ²²⁵Ac from ²²⁵Ra to produce additional ²²⁵Ac free from any potential ²²⁷Ac impurity.

1. Introduction

²²⁵Ac and ²²⁷Ac are promising isotopes for therapeutic nuclear medicine. ²²⁵Ac has been studied directly and as a source of ²¹³Bi for the treatment of various diseases (Muller et al., 2017). ²²⁷Ac is an important source of ²²³Ra used in approved treatments for metastatic castration-resistant prostate cancer which has spread to bone, Xofigo (Muller et al., 2017). Unfortunately, current sources of ²²⁵Ac, produced from legacy ²²⁹Th stocks separated from ²³³U breed reactor fuel, are not sufficient to support extensive trials or large scale treatment (Boll et al., 2005).

Other processes for the production of ²²⁵Ac or ²²⁹Th have been explored, including irradiation of highly radioactive ²²⁶Ra or ²³⁰Th targets (Zhuikov et al., 2011). One particularly promising route for the production of ²²⁵Ac is high energy proton spallation on ²³²Th (Harvey et al., 2009; Lefort et al., 1960; Tewes and James, 1952). While requiring relatively high proton energies for efficient production of

actinium, the ²³²Th spallation route offers the advantage of abundant, relatively low radioactivity target material. Additionally, proton spallation reactions on ²³²Th could also be a significant source of ²²⁵Ra, which could be utilized for the production of additional ²²⁵Ac, and ²²⁷Ac (Harvey et al., 2011; Radchenko et al., 2015).

Processes for the separation of actinium and radium from irradiated thorium targets often begin with the dissolution of thorium metal in nitric acid and traces of hydrofluoric acid, followed by solvent extraction or large anion exchange columns to remove the large mass of thorium (Aliev et al., 2014; Ermolaev et al., 2012; Harvey et al., 2011; Vasiliev et al., 2016; Zhuikov et al., 2011). These processes require large volumes of extraction solvent or anion exchange resin, high nitric acid concentrations, and may also require evaporations or other feed adjustments prior to further concentration and purification of the actinium fraction. Once the bulk thorium is removed, the actinium is further purified utilizing ion exchange and/or extraction chromatography to remove protactinium and light spallation byproducts.

* Corresponding author at: PG Research Foundation, 1955 University Lane, Lisle, IL 60532, USA.
E-mail address: dmcalister@eichrom.com (D.R. McAlister).

An alternative method dissolves the thorium target in hydrochloric acid with traces of hydrofluoric acid and converts the dissolution solution to citrate prior to selective extraction of actinium and radium using much smaller cation exchange resin columns (Mastren et al., 2017; Radchenko et al., 2015). This method offers the advantage much smaller chromatography columns and a less hazardous feed solution, but requires the evaporation of the dissolved target to dryness, prior to dissolution in citrate.

In this manuscript, the authors will describe a system in which metallic thorium target material may be directly dissolved in a sulfate medium which can be used as the feed for a cation exchange resin process that will selectively adsorb radium and actinium. This method does not require evaporation following target dissolution, utilizes a feed solution that is less hazardous than the 4–8 M HNO₃ utilized in the anion exchange or solvent extraction processes, and uses cation exchange columns 10–20× smaller than the anion exchange columns required in methods where Th is selectively retained. Following rinsing steps to remove residual thorium, the actinium and radium can be recovered in a small volume of 5 M HNO₃ which is directly processed on extraction chromatography columns to further purify and concentrate actinium. Actinium is obtained in high purity and high yield in a small volume of 0.1–2 M HCl.

2. Materials and methods

2.1. Reagents

Ammonium bifluoride, sulfuric acid, ammonium sulfate, and ammonium hydroxide were American Chemical Society (ACS) grade and used as received (Fisher Scientific). Nitric acid, hydrofluoric acid, and hydrochloric acid were trace metal grade and used as received (Fisher Scientific).

²²⁷Th and ²²³Ra were separated from ²²⁷Ac (Oak Ridge National Laboratory) as previously described (McAlister and Horwitz, 2011). ²²⁵Ac was separated from ²²⁹Th as previously described (McAlister and Horwitz, 2011). Thorium oxide (99.99%, Strem Chemical) and thorium metal powder (200 mesh, International Bio-Analytical Industries, Inc.) were used as received. A legacy supply of anhydrous thorium sulfate (Strem Chemical) was utilized as received, but no longer appears to be commercially available from this source. ¹³³Ba was obtained from Eckert and Zeigler. Standard solutions of 10 mg/mL thorium and barium were obtained from High Purity Standards.

Analytical grade cation exchange resin (200–400 mesh), UTEVA Resin (50–100 μm and 100–150 μm) and DGA Resin, Normal (50–100 μm) were obtained from Eichrom Technologies, LLC. DGA, Normal resin contains the extractant N,N,N',N'-tetraoctyl diglycolamide.

2.2. Measurements

²²³Ra, ²²⁷Th, ²²⁵Ac(²²¹Fr), and ¹³³Ba were measured using an Ortec GEM15–70 high purity germanium (HPGE) detector with DSpec LF digital signal processor. ²²⁵Ac was measured via its ²²¹Fr daughter after at least one hour of ingrowth/decay. ²³²Th was measured using an Agilent 4200 microwave plasma-atomic emission spectrometer (MP-AES). The pH of samples was measured using a combination electrode and AR25 dual channel pH/ion meter (Accumet).

Sulfate concentration was determined by addition of a known mass of barium (in molar excess of the sulfate concentration) as a 10 mg/mL standard solution spiked with ¹³³Ba tracer. After mixing for 30 min, the sample was centrifuged to settle the BaSO₄ precipitate. An aliquot of the supernate was measured by HpGe gamma spectroscopy. The sulfate concentration was calculated by difference from the ¹³³Ba spiked activity and activity remaining following BaSO₄ precipitation.

2.3. Thorium metal dissolution

No reference to the successful dissolution of thorium metal in sulfate media was found in the available literature. However, thorium oxide dissolution by fusion with sulfate salts has been thoroughly studied (Singh Mudher et al., 1999; Keskar et al., 2000). Experience with dissolution of thorium metal with nitric acid and preliminary experimentation suggested dissolution of thorium metal in sulfuric acid with a trace of HF should be possible.

A known mass of thorium metal powder was placed in a Pyrex glass beaker with a watch glass lid. A volume of 8 M sulfuric acid sufficient to yield the final desired sulfate concentration was added. As with dissolution with HNO₃, a small amount hydrofluoric acid was added to the sample to increase the dissolution rate. The sample was mixed on a stirring hotplate at room temperature for 5–10 min, and the temperature slowly ramped over 1 h to 80 °C. Deionized water was periodically added to control the temperature of the relatively exothermic dissolution reaction. Additionally, the volume of the solid material increases upon conversion to the sulfate, and the added water prevents the mixture from becoming too thick for adequate stirring. When enough deionized water has been added to reach the final volume, the sample was heated at 80–90 °C with mixing for one hour to ensure complete dissolution. As the sample was cooled to room temperature, a clear solution of thorium sulfate was produced. (The thorium sulfate is less soluble at higher temperatures.) The pH of the thorium sulfate solution was adjusted as needed (typically to pH 1.0 – 2.5) by the addition of ammonium hydroxide, and the solution was filtered through a 25 mm 0.45 μm PTFE syringe filter (Macherey-Nagel) to remove small traces of undissolved solids.

Observation of the dissolved thorium solution over a 2 week period and monitoring of spiked ²²³Ra and ¹³³Ba activities with 10⁻⁷ – 10⁻⁶ mol/L of stable Ba suggested the solution to be stable, with no indication of losses due to (Ra/Ba)SO₄ precipitation (K_{sp} Ba = 1.08E-10). The short half-lives of the radium and barium isotopes produced in the proton bombardment of thorium should preclude formation of sufficient mass to precipitate (Ra/Ba)SO₄. Precipitation should not be an issue as long as the thorium target material does not contain significant amounts of Ba impurity.

2.4. Dry weight distribution ratio measurements

Dry weight distribution ratio (Dw) measurements were performed as previously described (Horwitz et al., 2005) by adding a known mass of resin (10–50 mg) to a 7 mL borosilicate glass culture tube. For the cation exchange resin, the dry weight was determined by drying to constant weight at 80–90 °C. To the resin, a solution (0.5–1.0 mL) containing the radioactive tracer was added. Thorium sulfate solutions were prepared by dissolving anhydrous Th(SO₄)₂ in aqueous solutions of ammonium sulfate and sulfuric acid or by adjustment of thorium metal dissolved in H₂SO₄/HF. The solution and resin were equilibrated for 1–2 h on an orbital plate shaker. The samples were centrifuged, and an aliquot of the aqueous phase was removed and filtered through a 3 mm 0.45 μm PTFE syringe filter (Macherey-Nagel) to remove any residual solids. Aliquots of the filtered sample and the initial tracer solution were analyzed by HpGe gamma spectrometry. The Dw was calculated using the following formula:

$$Dw = [(A_0 - A_f) \cdot v] / [A_f \cdot m \cdot s]$$

where A₀ is the initial activity, A_f is the final activity (post equilibration), v is the volume of aqueous phase in milliliters, m is the mass of resin in grams and s is the ratio of dry resin (for hydrated ion exchange resins). Duplicate measurements typically agreed within 10% or roughly the size of the data points in the plots of Dw.

Download English Version:

<https://daneshyari.com/en/article/8208367>

Download Persian Version:

<https://daneshyari.com/article/8208367>

[Daneshyari.com](https://daneshyari.com)