

## Application of nuclear forensics methodology to americium

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The element Am has historically been underrepresented in the field of nuclear forensics, which focuses on the two elements critical to the current nuclear fuel cycle and nuclear weapons complex, U and Pu. <sup>241</sup>, <sup>243</sup>Am are daughters of <sup>241</sup>, <sup>243</sup>Pu respectively and byproducts of nuclear reactor operation and plutonium stockpiling, with <sup>241</sup>Am being both the primary grow-in contaminant in Pu stockpiles and a major long-lived reactor byproduct. Am could be attractive for proliferation and/or nuclear terrorism [1, 2] and it is widely available and used in multiple civilian industries [3], so this project seeks to adapt Pu-based nuclear forensics methods to Am.

Previous work at Texas A&M University has created a reactor-type discrimination methodology capable of identifying reactor type, time since irradiation, and fuel burnup for purified Pu samples based on actinide isotopic ratios and key fission product ratios [4-6]. Physical samples were irradiated and chemically processed to create purified Pu of known history to validate reactor modeling, which was done via decay radiation measurement and mass spectrometry, the latter of which required radiochemical separations to resolve isobaric overlap. The goal of this project is to modify this method for use with purified Am, which may contain the same forensic information as its parent Pu.

One of the two primary production routes of purified Am is as the byproduct of Pu stockpile regeneration, meaning that any trace forensic signatures remaining from the initial reactor production will have been reduced by at least two purification processes: once to create Pu, and then again to separate Am. As a result, a higher total mass of Am may be needed to have the same absolute level of trace elements as for Pu, which was already estimated to need 4-40 g [7]. <sup>241</sup>, <sup>243</sup>Am have much higher specific activities than <sup>239</sup>Pu, making the necessary amounts of Am for this project a radiation safety concern. Thus, work has focused on developing a procedure to separate bulk Am from the elements that require further chemical separations during the reactor-type discriminator method (Ce, Sm, Nd, and Eu).

An extensive literature search yielded multiple routes for separating Am from light lanthanides, a process made difficult by their strong similarities in chemistry. The initial method chosen for this project was a combination liquid-liquid/redox extraction using the ligand *N,N,N',N'*-tetraoctyl diglycolamide (TODGA) to extract lanthanides and sodium bismuthate as an oxidizing agent to produce Am(V), which is not extracted by TODGA [8]. This method was chosen for its high published separation factors and its overall speed, which reduces received dose. To tune the method for this specific project, and because additional details such as throughput and loading factors were not published, experiments were performed to validate the method and determine these missing factors.

The extraction method is performed in two steps: a pre-loading phase, and a liquid-liquid/redox combination. The pre-loading phase describes incorporating a strong Bi(V) oxidizing agent into a 0.1 M TODGA in n-dodecane solution by mixing this solution with equal volumes of 3 M HNO<sub>3</sub> with 15-20 mg of NaBiO<sub>3</sub> for two hours. This pre-conditions the TODGA solution and loads Bi(V) as bismuthic acid into the organic phase, creating the extractant to be used in the second step. The second step then begins with

a 3 M HNO<sub>3</sub> solution containing Am and lanthanides and is contacted with the pre-loaded extractant for 1 min while vortexing. All species initially extract into the organic phase, where Bi(V) oxidizes Am(III) to Am(V), which heavily favors back-extracting into the aqueous phase. Lanthanides are not oxidized and remain in the organic phase, enabling the separation of phases to complete the extraction.

The initial experiments following the published procedure as described failed to separate Am from Ln elements because all species remained in the aqueous phase, not the organic, as would have been predicted. During the pre-loading process, a large, gel-like third phase formed, and the lack of any Ln extraction indicated that this third phase complexed with all TODGA molecules. Follow-up experiments probed the effect of the amount of NaBiO<sub>3</sub> on the efficiency of the Am/Ln separation, shown in Table I as separation factors for Am from each Ln element tested. All Ln assays were done by ICP-MS and all Am assays were done by relative  $\gamma$ - or  $\alpha$ -spectrometry.

<b>Table I: Separation Factors for NaBiO<sub>3</sub> Concentrations</b>					
<b>NaBiO<sub>3</sub> Loaded (mg/mL)</b>	<b>SF<sub>Am,Ce</sub></b>	<b>SF<sub>Am,Nd</sub></b>	<b>SF<sub>Am,Sm</sub></b>	<b>SF<sub>Am,Eu</sub></b>	<b>SF<sub>Am,Gd</sub></b>
<b>5</b>	$(8 \pm 5) \times 10^{-5}$	$(1 \pm 9) \times 10^{-4}$	$(5 \pm 3) \times 10^{-4}$	$(1.0 \pm 0.61) \times 10^{-3}$	$(1.1 \pm 0.65) \times 10^{-3}$
<b>7.5</b>	$(6.4 \pm 2.2) \times 10^{-2}$	$0.30 \pm 0.11$	$0.94 \pm 0.50$	$1.43 \pm 0.76$	$0.36 \pm 0.14$
<b>10</b>	$0.14 \pm 0.10$	$0.83 \pm 0.65$	$4.7 \pm 3.4$	$8.4 \pm 5.8$	$3.4 \pm 1.7$
<b>20</b>	$0.20 \pm 0.55$	--	$3.0 \pm 8.2$	$6.1 \pm 17$	$10. \pm 28$

No concentration of NaBiO<sub>3</sub> enabled a successful extraction as shown in the literature. In addition, most experiments showed high variation across triplicate trials performed identically and simultaneously, making the method highly unreliable even if it had been successful. In place of this liquid-liquid method, focus has been shifted to testing alternative separation methods using column chromatography [9, 10]. These methods are considered more reliable but may sacrifice some of the speed advantages the TODGA system boasted. The first of two literature column schemes identified as viable has begun testing, with a goal of optimizing separation efficiency and speed.

Work has been done to acquire large Am samples for use once the above method is finalized. An aged 0.2 mCi <sup>243</sup>Am sample from the National Institute of Standards and Technology (NIST) was acquired in June 2025 for use in this project. A second sample of aged Pu with significant Am grow-in may be available through NIST.

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