

## Application of nuclear forensics methodology to americium

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The elements U and Pu are the primary focus of academic nuclear forensics research, with minor actinides and other radioactive materials underrepresented. Am, the primary contaminant in Pu sources and the daughter of <sup>241,243</sup>Pu, is one such underrepresented material that happens to be widely proliferated. Used at scale by private industry [1] and widely available to the general public in small quantities contained in smoke detectors [2], Am receives little direct nuclear forensic attention despite its potential for proliferation [3, 4]. This project aims to expand the capability of nuclear forensics *vis-à-vis* Am by adapting an existing source-reactor type discrimination method for plutonium, based on radiochemical measurements of actinide and intra-elemental fission product isotopic ratios. We will also work with Dr. Sunil S. Chirayath at Oak Ridge National Laboratory to apply the existing methodology to Am samples.

First, the needed mass of Am must be determined. Previous work in the Folden group estimated the mass of Pu needed for a reactor-type discrimination method was 4–40 g [5]. This estimate may not be accurate for Am because purity standards for Am used by the Department of Energy are less stringent than those for Pu [6], and common Pu reprocessing schemes see Am go into the same streams as most fission products, leading to a possible concentration effect. The starting mass of americium required for an investigation is inversely proportional to the concentration of trace fission products, such that milligrams of Am would be needed if the concentration of fission products per mass of americium were in the ppb range [7]. Alternatively, if concentrations were at the legal limit of the Department of Energy's guidance to the former Rocky Flats plant [6], nanograms of Am would contain fission product levels measurable by mass spectrometry [7]. Conservatively estimated, tens of milligrams of Am may be needed, which corresponds with up to 100 mCi of activity. The concentration of fission products is inversely related with the quality and quantity of purifications performed throughout a sample's history, which in a forensic investigation is typically unknown.

We have begun a collaboration with Pacific Northwest National Laboratory to study legacy Am samples that may have forensic value. For these legacy samples, no information on sample history is available and the possibility that these estimates are not conservative enough cannot be discounted. Designs that minimize the danger of handling these levels of activity have been made with input from EHS experts at Texas A&M and collaborators at PNNL.

This project will adapt previous work at Texas A&M that developed a source-reactor type discrimination method for purified Pu samples, using intra-elemental isotopic ratios, and apply it to Am samples. These ratios are taken on a suite of elements including any present actinides (Pu, Am) and key fission products, including Cs and multiple lanthanide elements (Sm, Eu); the method is flexible enough to incorporate some additional fission product elements, if present in a sample. If measured, these ratios can be used in conjunction with a library of reactor simulations to determine reactor-type, burnup, and time since irradiation. A critical step to this process is the partitioning of the lanthanides, as they exhibit isobaric interferences that cannot be resolved in traditional mass spectrometers. However, Am and

lanthanides behave similarly in most chemical systems due to similar oxidation state preferences (+3) and atomic radii [8, 9]. The primary challenge to adapting the reactor-type discrimination method to Am samples is the separation of high activities of Am from trace fission products, to enable the partitioning of the lanthanides in a safe manner.

We are developing two research plans for the extraction of lanthanide fission products from the Am sources at PNNL. The preferred method is a modification of a rapid liquid-liquid extraction method [9]. Under strong oxidizing conditions, Am has access to a +5-oxidation state that the select lanthanide fission products of value do not have. Using the tridentate extracting ligand TODGA that strongly extracts +3 oxidation state elements mixed with a strong oxidizer such as Bi (V), the fission products are extracted into an organic phase and Am remains in the aqueous. This method has been shown to have extremely high separation factors in single contact-cycles lasting under 60 seconds. Development of a method for the back-extraction of lanthanide elements from this TODGA extractant system is currently underway. An alternative method using a TEVA column chromatography resin with a ammonium thiocyanate eluent system is also being considered [10].

Either route achieves the separation of trace analytes from Am at PNNL facilities, yielding fractions ready for lanthanide partitioning via  $\alpha$ -HIB column chromatography [5], followed by quantification via ICP-MS. Intra-elemental ratios of fission products, Am, and Pu will then be used in the reactor-type discrimination library methodology, ultimately yielding information on the source-reactor type that initially created PNNL's legacy Am.

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