

## Relative formation probabilities for fluoride and oxyfluoride anions of U, Np, Pu and Am in accelerator mass spectrometry measurements at VERA<sup>†</sup>

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Atomic anions of actinides are not formed efficiently in a Cs sputter ion source, so they must be extracted as molecular anions for AMS measurements.<sup>1)</sup> Fluoride anions were introduced as an alternative to the oxide anions previously established for this purpose.<sup>2)</sup> Some potential benefits of fluoride extraction of actinides have already been reported: Fluorine is monoisotopic, fluoride anions have the potential for increased ionization yields in low cesium flux ion sources,<sup>2)</sup> could reduce the hydride background<sup>2)</sup> and show some degree of elemental selectivity.<sup>3)</sup> Furthermore, fluoride and oxyfluoride molecular anions could also be of use in isobar separation techniques such as Ion Laser InterAction Mass Spectrometry (ILIAMS)<sup>4)</sup> or the Isobar Separator for Anions (ISA).<sup>5)</sup> The efficiency with which an anion species is formed in the sputter process is determined by the electron affinity of the corresponding neutral atom or molecule.<sup>1)</sup> The stability of an anion against photodetachment in systems like ILIAMS is in turn also related to this electron affinity.

Developing such isobar separation methods in the actinide range could open up new possibilities for the study of actinides in the environment, such as new potential isotopic spikes for normalization or an extended multi-actinide analysis with simplified chemistry from a single AMS sample.

Based on estimates of the releases from nuclear tests and reprocessing plants, <sup>237</sup>Np is thought to be the second most abundant anthropogenic actinide in the environment.<sup>6)</sup> <sup>237</sup>Np exhibits conservative behavior in natural waters as it mainly exists in the highly soluble Np(V)O<sub>2</sub><sup>+</sup> form under oxidizing conditions<sup>7)</sup> and has a long half-life ( $T_{1/2} = 2.1 \times 10^6$  y). These two properties could turn <sup>237</sup>Np into a valuable tool for tracking environmental processes such as water mass transport.<sup>8,9)</sup> The main obstacle to establishing <sup>237</sup>Np as an environmental tracer is the lack of an isotopic spike material for a matrix independent and reliable normalization of <sup>237</sup>Np measurements by mass spectrometric methods.

For this purpose, <sup>236</sup>Np was produced via the <sup>232</sup>Th(<sup>7</sup>Li, 3n)<sup>236</sup>Np reaction at the RIKEN Nishina Center. In addition to the desired <sup>236g</sup>Np, isobaric contamination can arise either from <sup>236</sup>U produced by neu-

tron capture on <sup>235</sup>U impurities in the irradiation target, or from the decay of metastable <sup>236m</sup>Np to <sup>236</sup>U or <sup>236</sup>Pu, so further analysis of the mass 236 fraction was required.

The relative formation probabilities of AnF<sub>5</sub><sup>-</sup>, AnF<sub>4</sub>O<sup>-</sup>, AnF<sub>3</sub>O<sub>2</sub><sup>-</sup>, AnF<sub>4</sub><sup>-</sup>, AnF<sub>3</sub>O<sup>-</sup> and AnF<sub>2</sub>O<sub>2</sub><sup>-</sup>, with An representing the actinides U, Np, Pu or Am, have been investigated. The AnF<sub>4</sub><sup>-</sup>/AnF<sub>5</sub><sup>-</sup> ratios of these actinides have been shown to be element-specific within each measurement, with an order of magnitude separating the AnF<sub>4</sub><sup>-</sup>/AnF<sub>5</sub><sup>-</sup> ratios from one actinide element to the next. The magnitude factor is robust and reproducible. Based on these findings, the AnF<sub>4</sub><sup>-</sup>/AnF<sub>5</sub><sup>-</sup> ratio serves as an elemental fingerprint. A significant amount of isobaric interference would shift this ratio relative to the reference ratio for the actinide of interest as determined on calibration samples in the same measurement. The prospective neptunium spike material provided a first application for this kind of isobar analysis, and the tentative first results are compatible with a successful production and chemical separation of <sup>236</sup>Np.

Choosing the tetrafluoride system molecular anions for the extraction of Np and U suppresses the interfering isobar <sup>236</sup>UF<sub>4</sub><sup>-</sup> by an order of magnitude compared to <sup>236</sup>NpF<sub>4</sub><sup>-</sup> in the ion source. The large number of (oxy) fluoride anions of various actinides greatly enhances the possibility of finding suitable molecular ion systems for isobar separation using methods such as element-selective photodetachment in ILIAMS.

### References

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