Source reactor-type of irradiated UO_2 using ultra-high-resolution mass spectrometry

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The field of pre-detonation nuclear forensics seeks to determine the origin, intended application, and potential threat of interdicted nuclear and radiological materials [1]. Given the increasing concern surrounding nuclear proliferation and terrorism, there is a critical need for rapid, accurate forensic techniques. Nuclear forensic methodologies exploit the physical, chemical, and isotopic characteristics of materials to reconstruct their history. Traditional analyses require chemical separations to mitigate isobaric interferences prior to isotopic measurements [2]. In this study, ultra-high resolution mass spectrometry is employed to characterize irradiated uranium dioxide samples without chemical separations, with the objective of evaluating intra-elemental fission product isotopic ratios relevant to source reactor attribution.

Three UO_2 fuel pellets with varying compositions and irradiation histories were analyzed. In 2013, a disc composed of depleted UO_2 (DUO_2) sheathed in gadolinium was irradiated at the High Flux Isotope Reactor (HFIR). Following dissolution and forensic characterization, this disc was determined to have reached a burnup of 4.67 GWd/MTU. In 2016, a second irradiation was conducted at the Missouri University Research Reactor (MURR), involving a disc composed of natural UO_2. This sample was irradiated to a burnup of 0.97 GWd/MTU. In 2021, a third irradiation at MURR utilized low-enriched UO_2; this sample, referred to as MURR #1, was irradiated to a burnup of 0.944 GWd/MTU [4].

Initially gamma spectrometry was performed to identify gamma-emitting fission products within each sample. Subsequently, in collaboration with Clemson University, 1 mL aliquots from each sample—untreated by chemical separation or dilution—were analyzed using ultra-high resolution mass spectrometry. This technique employed an Orbitrap instrument coupled with a Booster module. The Booster enhances sensitivity and resolution by enabling dual acquisition of spectral data. Analytical conditions included a maximum injection time of 230 ms, an automatic gain control (AGC) target of 10^6, and 2% HNO_3 as the carrier solution.

Uranium isotopic ratios were measured to verify the uranium composition of each sample. Three 20 μL injections per sample were analyzed at a resolution of 70,000 (m/Δm). The resulting $^{235}U/^{238}U$ ratios are summarized in Table I.

Table I. Measured uranium isotopic ratios. RSD is the relative standard deviation.

Sample	$^{235}U/^{238}U$ Average (%)	RSD (%)
HFIR	0.276(6)	2.3
MURR C	0.619(35)	5.7
MURR	3.559(6)	0.2

For lanthanide isotopic analysis, samples were directly infused into the mass spectrometer and analyzed at a resolution of 230,000 [3]. A primary analytical challenge was the isobaric interference between ^{150}Sm and ^{150}Nd. However, the high-resolution capability of the instrument enabled full separation of these isobars, permitting accurate intra-element samarium isotopic ratio determination. The resulting samarium isotopic ratios are presented in Table II.

Table II. Samarium Intra-Element Isotopic Ratios Measured.

Isotope Ratio	HFIR	MURR C	MURR
$^{150}Sm/^{149}Sm$	3.721	2.926	1.706
$^{152}Sm/^{149}Sm$	3.197	2.945	0.497
$^{150}Sm/^{152}Sm$	1.164	0.993	3.430
$^{152}Sm/^{154}Sm$	4.941	1.033	1.634

The results demonstrate significant variation in isotopic ratios across the three fuel samples, which is consistent with their distinct irradiation environments and histories. The measured $^{235}U/^{238}U$ ratios vary significantly, reflecting differences in different levels of enrichment and burnup. Notably, the MURR sample shows the highest $^{235}U/^{238}U$ ratio, consistent with its relatively low burnup and initial enrichment estimation of ~3.44%. The successful resolution of ^{150}Sm from ^{150}Nd is critical for obtaining accurate samarium isotopic ratios. Specifically, the $^{150}Sm/^{149}Sm$ and $^{150}Sm/^{152}Sm$ ratios are particularly informative for reactor-type discrimination due to their sensitivity to neutron flux and fuel residence time, respectively. These isotopic signatures serve as forensic indicators of reactor type, neutron energy spectrum, and fuel history.

The ability to acquire high-fidelity isotopic data without chemical separation underscores the potential of ultra-high resolution mass spectrometry as a rapid, low-preparation tool for nuclear forensic analysis. Future work will focus on analyzing additional irradiated UO_2 samples using this technique to

further develop intra-elemental isotopic ratios that can support attribution of unknown nuclear materials to specific reactor types or operational conditions.

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