



Secondary ion mass spectrometry signatures for verifying declarations of fissile-material production



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HIGHLIGHTS

- Direct analysis of uranium enrichment facility components using SIMS.
- U, O and F signatures from a pipe piece located within an enrichment facility.
- Isotopic analysis determined enrichment of $^{235}\text{U}/^{238}\text{U}$ ratio to 0.0116 ± 0.0019 .
- SIMS depth analysis was isotopically homogenous to a depth of $\sim 23.5 \mu\text{m}$.
- Optical profilometry measurements determined a sputter rate of 0.48 nm/s for 18.5 keV O^- ions.

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ABSTRACT

Direct analysis of uranium enrichment facility components were performed using secondary ion mass spectrometry (SIMS). A standard protocol was developed to enable preparation of SIMS samples from a corroded pipe piece without disturbing the corrosion layer. Unique uranium, oxygen and fluorine containing signatures were discovered in the corrosion layer by performing a mass scan of the region of interest from 230 to 280 amu. These signatures identified the source of the corrosion layer as uranium hexafluoride (UF_6) or an associated hydrolysis product. Isotopic analysis of the corrosion layer determined enrichment of ^{235}U to a value of 0.0116 ± 0.0019 for the $^{235}\text{U}/^{238}\text{U}$ isotopic ratio as compared to the NIST traceable standard (CRM 112-A) with a natural $^{235}\text{U}/^{238}\text{U}$ isotopic ratio of 0.007254 ± 0.000004 . SIMS depth analysis revealed that the corrosion layer was isotopically homogenous to a depth of $\sim 23.5 \mu\text{m}$. Optical profilometry measurements prior to and following SIMS depth analysis were used to determine a sputter rate of 0.48 nm/s for 18.5 keV O^- ion bombardment of the corrosion layer. The data presented is conclusive evidence that SIMS depth analysis can be used to identify novel nuclear archeology signatures from uranium enrichment components and perform meaningful isotopic analysis of these signatures.

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1. Introduction

The Nuclear Non-Proliferation Treaty (NPT) and other efforts to block the spread of nuclear weapons have created the need for a variety of verification technologies (Gavron, 2005; Lyakhova et al., 2013; Miley et al., 2009; Schwaiger et al., 2002; Stocki et al., 2005). These methods aim to support the International Atomic Energy Agency's (IAEA) safeguards efforts in verifying declarations of fissile material production at declared facilities. This validation process, often termed nuclear archeology (Fetter, 1993; Schwantes et al., 2009; Wood et al., 2014), is of great importance to the nonproliferation community responsible for monitoring a growing number of uranium enrichment facilities worldwide. The most

difficult part of verifying special nuclear material production is obtaining an analytical signature that is not only indicative of the current enrichment campaign, but also seeks to characterize the complete history of prior cascade configurations. In most cases, acquisition of nuclear materials from within enrichment facilities is critical to treaty verification. Chemical compounds (UF_6 , UO_2F_2 , HF, etc.) used in uranium enrichment facilities are highly reactive and can corrode metal components (i.e. centrifuges, pipes, valves, etc.) (Saniger et al., 1990; Wang et al., 1991). Theoretically, corrosion layers on enrichment facility hardware contain unique isotopic signatures that can be used to establish operational history. Nuclear archeology aims to identify these signatures, accurately and precisely measure them and create computational models that translate the measured data into a record of the fissile-material production.

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A robust measurement technique for determining the operational history of an enrichment facility does not currently exist. A proposed methodology must meet several criteria in order to be effective. The method would ideally be a technique capable of high abundance sensitivity, atomic and molecular specificity and provide high precision and accurate isotopic data. Additionally, sample heterogeneity both spatially and in depth must be preserved to locate unique signatures. Similar signatures for environmental sampling have previously been identified by SIMS analysis of swipe materials (Ranebo et al., 2009; Tamborini, 2004); however, these methods do not preserve depth information, allowing only for the identification of rare particles that may be representative of historical operations or clandestine activity. The methodology purposed herein aims to preserve the sample heterogeneity in depth and is, therefore, more suitable because signatures of interest are not diluted. This method is a way to access more information than was previously available with other SIMS techniques. Although many radiometric analysis techniques have proven to be useful in similar analyses, mass spectrometry is ideal for the identification and measurement of nuclear archeology signatures (Fetter, 1993; Schwantes et al., 2009; Wood et al., 2014, 2002).

SIMS provides a useful method to exploit isotopic signatures resident in enrichment facility equipment and assists in determining an estimate of the enrichment levels and operational history. SIMS is a mass spectrometry technique that uses high energy primary ions to generate secondary ions indicative of the isotopic composition of solid samples. These secondary ions are extracted into a mass spectrometer where they are separated by their mass-to-charge ratios. In addition, SIMS has been used to provide the isotopic composition of a sample as a function of depth (Marchand et al., 2013; Pizzi et al., 2012; Ranebo et al., 2007). SIMS is, therefore, a powerful analytical method for uncovering embedded isotopic information via depth profiling. A SIMS-based technology for validating the enrichment production history of declared facilities could have valuable application for resolving international concerns associated with an ever-growing number of uranium enrichment facilities.

A possible scenario where SIMS could provide valuable information about the operational history of a declared enrichment facility is as follows. A hypothetical uranium enrichment facility was operated over 10 years, producing civilian sector nuclear fuel with a ^{235}U enrichment of 3%. Over this duration, UF_6 within the facility interacted with the metal components of the enrichment facility generating a corrosion layer primarily composed of uranyl fluoride (UO_2F_2) and uranium sub-fluorides (UF_4 , U_2F_9 , UF_5 , etc.). The growth of this corrosion layer decreases exponentially from the time of the first exposure of the bare metal components to the UF_6 . After this initial period of civilian operation, the enrichment facility was reconfigured to run as a research reactor and operated for 6 months producing uranium with a ^{235}U enrichment of 20%. The facility was subsequently reconfigured to its original state, once again, producing civilian sector nuclear fuel at 3% for an addition 5 years. Any metal components that were in contact with UF_6 throughout these reconfiguration periods would have a corrosion layer mainly composed of uranium compounds with a ^{235}U enrichment of 3%, but with a buried layer of corrosion products with a ^{235}U enrichment of 20%. SIMS depth analysis of the corrosion layer could reveal an isotopic distribution first of ^{235}U enrichment of 3%, then a thin layer of 20% ^{235}U enrichment, then back to 3%. In this way, SIMS depth analysis could be used to verify the enrichment production history of this declared facility accurately identifying the period of time for which the facility was operated as a research reactor. In addition to information about the sequence of different ^{235}U enrichment exposures, if the growth rate of the corrosion layer was well known and adequately characterized, specific information about the individual exposure times could be obtained.

2. Experimental

The enrichment facility component analyzed consisted of a stainless steel pipe that retained a layer of material (corrosion layer) on the inside surface; this internal portion of the pipe was exposed to an unknown set of nuclear processing conditions. Sub-samples were cautiously extracted from the pipe without disturbing the corrosion layer by drilling 1/3 in. discs from the side, using a hole-saw (Fig. 1a). Because the pieces sampled from the pipe had a finite diameter, a slight curvature could be seen in the resulting sample. Although curved samples typically present difficulties for SIMS analysis, the curvature over the area of interest proved to be minimal. Moderate use of a mechanical file along the cut edges of the disc aided the reduction of burred edges and ensured a relatively flat surface for analysis when mounting. The sample discs were then mounted in a typical CAMECA SIMS sample holder, shown in Fig. 1b and entered into the vacuum chamber without further sample preparation.

Prior to SIMS analysis, radiometric counting was performed on the samples and no detectable uranium signals were measured. The radiometric counting measurements were taken with a 70% relative efficacy coaxial high purity germanium detector (HPGe) by Ortec. This detector is classified as low background; meaning that the materials used for construction are screened for radio-purity and the system is constructed in a manner to reduce background signals from the detector assembly itself. The detector is cooled with liquid nitrogen and cryostat controlled. The data from the detector was acquired using a Canberra Lynx digital signal processor and analyzed using the Canberra Genie2000 gamma analysis software suite.

SIMS analysis was performed on the upgraded CAMECA ims-4f at Pacific Northwest National Laboratory; a general description for the ims-4f instrument can be found in detail elsewhere (Meuris et al., 1989; Migeon et al., 1989). Briefly, the CAMECA ims-4f is a dynamic SIMS instrument that can be operated in both ion microscope (lower current, larger field-of-view) and microprobe (higher current, smaller field-of-view) modes. The SIMS analysis presented herein was performed with a duoplasmatron ion source generating O^- ions at 12.5 kV. The secondary ions resulting from primary ion sputtering were accelerated with a 6 kV positive bias on the sample, resulting in impact energy of 18.5 keV. Sputtered ions pass through an electrostatic analyzer and are then magnetically separated as a function of their mass-to-charge ratio; the secondary ion image field was 150 μm . The data collected for this report was obtained exclusively using an electron multiplier.

Pre- and post-SIMS analysis topographical measurements were performed by an optical profilometer (AEP Technology NanoMap 1000 wli 3D). These measurements were made using a 150 \times 150 μm field-of-view and medium ($\sim 1.0 \mu\text{m}$) optical resolution. Analysis of the surface roughness was made prior to SIMS depth analyses to characterize the initial topography of the corrosion layer. Measurements of the SIMS depth analysis craters were performed following the isotopic measurements of the samples in order to provide information about the measured depth as well as the sputter rate of the SIMS depth analysis.

3. Results and discussion

The initial SIMS analysis of the pipe piece focused on obtaining mass spectra from the corrosion layer in order to determine the presence of any unique nuclear archeology signatures. The mass spectra were obtained by scanning the magnet and measuring the ion counts as a function of mass-to-charge ratio. A representative mass spectrum of the corrosion layer is shown in Fig. 2. This mass spectrum, representing a mass range from 230 to 280 amu, was

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