



Spatial distribution of uranium isotopes in solid nuclear materials using laser ablation multi-collector ICP-MS

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ABSTRACT

Employing laser ablation multi-collector ICP-MS (LA-MC-ICP-MS), its potential for evaluating the homogeneity of solid uranium (U) bearing materials was investigated. To this end, the $n(^{235}\text{U})/n(^{238}\text{U})$ ratio of two low-enriched U certified reference materials (CRMs), i.e. powdered standard reference material U-010 (~1 wt% ^{235}U) and a UO_2 pellet of CRM 125-A (~4 wt% ^{235}U) was determined using line scan analysis. Four spots of 5 μm diameter each were ablated per second with the LA system moved at a speed of 20 $\mu\text{m s}^{-1}$ for several minutes. Experimental and certified U isotope ratios matched perfectly, unequivocally validating the accuracy of the applied analytical methodology. In addition, the narrow and symmetric frequency distribution of the $n(^{235}\text{U})/n(^{238}\text{U})$ ratio of both CRMs confirmed their homogeneity with respect to the U isotopic composition. Utilizing LA-MC-ICP-MS line scan analysis of two similar UO_2 pellets (~1 wt% ^{235}U) from the 5th Collaborative Materials Exercise (CMX-5) revealed diverse inhomogeneity regarding their $n(^{235}\text{U})/n(^{238}\text{U})$ ratio. Although both UO_2 pellets used for the CMX-5 exercise were prepared from identical source materials, their different production routes yielded largely contrasting frequency distributions of the $n(^{235}\text{U})/n(^{238}\text{U})$ ratio. While ^{235}U isotope abundance ranged from 0.75%–1.6% for the first pellet, this value fluctuated between 0.45% and 3.0% for the second pellet. This specific information sheds additional light on the production process of these materials and is helpful in nuclear forensics investigations when determining the origin of unknown nuclear material. The depleted nature (~0.4 wt% ^{235}U) of two seized U metal samples was established through LA-MC-ICP-MS analysis of the $n(^{235}\text{U})/n(^{238}\text{U})$ ratio. As black and yellow regions within both U bearing samples had identical U isotopic composition, the observed colour differences might arise from different degrees of U oxidation and are not associated with U isotopic inhomogeneity within the material. The significantly different ^{235}U abundance of the two samples (0.3670 \pm 0.0015 wt.% and 0.4146 \pm 0.0013 wt.%), however, clearly indicates they were prepared from different source materials and/or from diverse amounts of them.

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1. Introduction

Nuclear forensic science, referred to as nuclear forensics, aims at identifying the origin of nuclear material found out of regulatory control [1]. More specifically, scientific analysis, focussing on nuclear or other radioactive material, or on other evidence that is contaminated with radioactive material, seeks for clues on its intended use and history [2]. Nuclear forensics additionally plays an important role in nuclear security regimes to prevent and respond to nuclear security events such as illicit trafficking of nuclear material. To this end, nuclear forensics utilizes material properties, so-called *signatures* that are inherent to the material and help revealing its processing history [1,2]. In this context, several measurable parameters are considered, such as isotope abundance ratios of lead, strontium, neodymium, sulphur, plutonium and uranium (U), the concentration of particular trace elements, as well as

daughter products of radioactive decay used for radiometric age dating [1–4].

In nuclear forensic investigations the determination of U isotopic signatures plays a key role. Although the minor U isotopes ^{234}U and ^{236}U also carry meaningful information, the $n(^{235}\text{U})/n(^{238}\text{U})$ ratio provides the level of U enrichment [1,2,5,6] which is, in many cases, the key parameter for decision if the possession of the material is consistent with legal requirements (e.g. natural U, low-enriched U or highly enriched U). Besides gamma spectrometry and thermal ionization mass spectrometry (TIMS), inductively coupled plasma-mass spectrometry (ICP-MS) is increasingly being applied for U isotopic analysis. While time-of-flight [7] and single collector [5,8–15] mass spectrometers have been employed repeatedly, ICP-MS instruments with multiple detectors steadily gain attraction for this purpose [6,15–20]. Also in nuclear forensics, laser ablation (LA) may serve as a powerful tool for sample introduction into the ICP-MS [16–20]. As only very small portions of the sample are required for LA-based analysis, the evidence, i.e. the solid sample, is available for further destructive analysis or can be archived

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for future analysis. Furthermore, the measurement can be completed rapidly (within a few hours), thus providing quick information to the investigating authority.

Irrespective of the measurement technique employed for analysis, the correct interpretation of the experimental data and the final conclusions rely on high quality analytical results. The regular participation in inter-laboratory comparison programmes (ILCPs) is beneficial to check the performance of the enrolled laboratories for a specific measurement parameter and helps detecting weak points in the applied analytical process. Our laboratory has been taking part in various ILCP for >20 years, further demonstrating the accuracy of its analytical data and fitness for purpose of the analytical procedures.

The Nuclear Forensics International Technical Working Group (ITWG) has repeatedly organized Collaborative Materials Exercises (CMXs) on sample materials such as plutonium oxide powder, low and highly enriched U as metal, powder or pellets [15,21,22]. These samples reflect the types of specimens that are frequently dealt with in a nuclear forensics laboratory. While CMXs are not intended to serve as proficiency tests for the participating laboratories, they were developed in order to provide a common problem set from which nuclear forensic techniques and methods can be compared and prioritized, establishing consensus decisions by the CMX participants.

The fifth and most recent exercise of this series, CMX-5, involved two low-enriched uranium oxide (UO₂) pellets [23]. The accurate determination of the U isotopic composition of each of these pellets was one of the requested parameters. As initial results needed to be reported within 24 h after receipt of the test samples, a first screening of the abundances of ²³⁴U, ²³⁵U, and ²³⁸U was performed on the entire solid samples using high resolution gamma spectrometry. These measurements provided a first helpful indication that the abundance of ²³⁵U of each of the two UO₂ pellets is slightly enriched (~1 wt%). Two restrictions, however, limit the significance of this initial finding. First, the combined relative uncertainty of the initial results (obtained by gamma spectrometry), amounting to about 15%, was relatively high. Secondly, as the entire sample is measured, only the average U isotopic composition of the pellets was obtained. The gamma spectrometry results are only meaningful, if the investigated pellets are homogeneous with respect to their U isotopic composition.

The main aim of the present study was the development and validation of an alternative “non-destructive” procedure for the accurate, precise and rapid determination of the U isotopic composition of U materials using LA-MC-ICP-MS. Results presented here highlight the significance of spatial resolution of such analysis that unmistakably reveal the (in-) homogeneity of the U isotopic composition of pressed U powder, UO₂ pellets and fragments of U metal.

2. Experimental methods

2.1. Instrumentation

All isotopic measurements were carried out with a NuPlasma™ (NU Instruments, Oxford, United Kingdom) double-focusing multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS). For U isotope ratio measurements the instrument was operated in low mass resolution mode ($R = 300$) with the major U isotopes (²³⁵U and ²³⁸U) measured on Faraday detectors, while ion counters were employed for the low abundant U isotopes (²³⁴U and ²³⁶U). As the $n(^{235}\text{U})/n(^{238}\text{U})$ ratio is the most important parameter for the principal aim of this study, the main focus is set on this U isotope ratio rather than on the minor ones, i.e. $n(^{234}\text{U})/n(^{238}\text{U})$ and $n(^{236}\text{U})/n(^{238}\text{U})$, respectively.

Sample introduction into the MC-ICP-MS was performed for aqueous samples via a T-connection through an Aridus II desolvating nebulizer (CETAC Technologies Inc., Omaha, NE, USA) or through a NWR-213 laser ablation unit (ESI, Huntingdon, UK) in the case of solid samples. The ns-LA system was equipped with a two-volume cell (a so-called TV2 cell) largely helping to prevent cross-contamination from

other samples within the LA chamber. The generated plume was transported from the LA cell to the MC-ICP-MS plasma using a laminar flow of Ar gas. Further details on the optimized instrumental settings as well as on the applied data acquisition parameters are reported elsewhere [20].

2.2. Reagents and standards

High-purity water (18.2 MΩ cm) from a water purification system (ELGA LabWater, Veolia Water Technologies, Celle, Germany) and sub-boiled nitric acid were used for the preparation of all solutions. The multi-element solution IV from Inorganic Ventures (Christiansburg, USA) was employed at a concentration of 50 ng g⁻¹ for daily optimization of the performance of the MC-ICP-MS. In liquid mode mass bias was measured with a 10 ng g⁻¹ solution of the isotopic reference material CRM U-500 (New Brunswick Laboratory, NBL, Argonne, IL, USA) isotopic reference material, while CRM U-020 (New Brunswick Laboratory, Argonne, IL, USA) was used to check the measured U isotope ratios. CRM solutions were prepared by dissolving an aliquot of the solid reference material in 8 M nitric acid with gentle heating. For LA analysis, a pellet of CRM U-020 was used to measure the mass bias factor and to calculate the gains of the employed ion counters. The accuracy of measurements was checked through repeated analysis of a pellet of CRM U-010 (New Brunswick Laboratory, Argonne, IL, USA). Further details on the measurement have been reported previously [20].

2.3. Investigated samples

The spatial distribution of the U isotopic composition was assessed with LA-MC-ICP-MS involving various solid U bearing materials, including certified reference materials (CRMs) and U samples, containing either depleted or low-enriched U: (a) a portion of the powdered CRM U-010 (NBL, Argonne, IL, USA) was pressed into a pellet with an X-PRESS hydraulic laboratory press (Spex Industries, Metuchen, USA) applying a force of 2 tons for 8 min. This way, stable pellets were produced without using any kind of additional binder. This U₃O₈ pellet with a diameter of 5 mm and ~1 mm height was subsequently subjected to LA-MC-ICP-MS. (b) CRM 125-A consisted of a sintered low-enriched (~4%) uranium oxide (UO₂) pellet with a mass of ~5.4 g. The batch of pellets had been prepared by Westinghouse Commercial Nuclear Fuels Division (Columbia, SC, USA) and chemically characterized by NBL [5]. Both CRM U-010 and CRM 125-A are certified for their U isotope amount ratio together with the respective uncertainties at the 95% level of confidence. (c) two UO₂ pellets from the 5th Collaborative Materials Exercise (CMX-5) organized by ITWG [23], and (d) two seized illicit U samples, here referred to Sample A and Sample B, respectively.

2.4. Measurement procedures

After daily optimization of the MC-ICP-MS performance using aqueous calibration solutions, no more liquid samples were aspirated through the desolvating nebulizer. Instead small (~5 μm) spots were subsequently ablated with the laser from solid samples placed in the LA chamber. The T-connection between the desolvating nebulizer and the LA system allowed the immediate switching between liquid and solid sample introduction [20]. The particle cloud generated by LA was transported via a laminar argon gas stream to the inductively coupled plasma, where particles were atomized and ionized before entering the mass spectrometer. The U isotopic abundances of actual solid samples were determined by both single spot and line scan analysis. For single spot analysis, 5 μm or 8 μm spots were ablated at a frequency of 4 Hz for a period of 5 s. The applied fluence (laser power) was varied between 2 and 4 J cm⁻² to adjust the ²³⁸U ICP-MS signal not to exceed 10 V that would otherwise cause saturation of the Faraday detector.

Line scan analysis was performed ablating spots with a diameter of 5 μm. The focussed laser beam was moved across the surface of the

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