LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

LLNL-TR-742611

Argentina-LLNL-LANL Comparative Sample Analysis on UO2 fuel pellet CRM-125A for Nuclear Forensics

R. Kips

December 1, 2017

Disclaimer

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

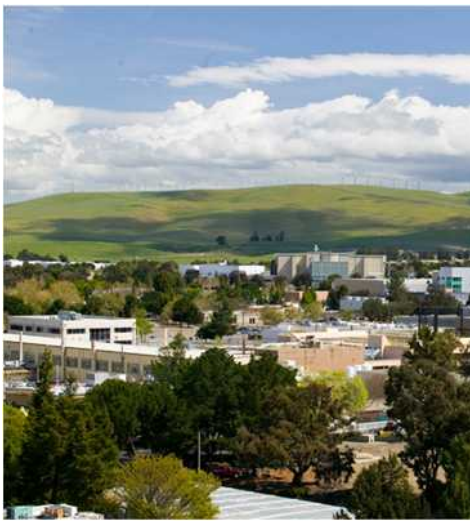
LLNL-TR-

Lawrence Livermore National Laboratory

Argentina-LLNL-LANL Comparative Sample Analysis on UO2 fuel pellet CRM-125A for Nuclear Forensics

Prepared by: TBD

November, 2017



Disclaimer

Table of Contents

1 Project Background

1.1 Argentina/DOE NSDD Bilateral Engagement on Nuclear Forensics

The U.S. DOE/NNSA's Office of Nuclear Smuggling Detection and Deterrence (NSDD) is cooperating with Argentina on strengthening Argentina's nuclear forensics capabilities.

- In February 2017, the Ezeiza Atomic Research Center hosted NSDD's Analytical Plan Development Workshop. In this scenario-based workshop, the participants worked through a fictitious nuclear forensics investigation, based on the CMX-4 exercise organized by Nuclear Forensics International Technical Working Group (ITWG).
- In August 2017, LLNL hosted the 14th Argentina-U.S. Joint Standing Committee on Nuclear Energy Cooperation (JSCNEC) at the Livermore Valley Open Campus (LVOC). This was the 14th consecutive meeting since its creation in 2003, reflecting the deep interest of both Argentina and the United States in strengthening cooperation in the field of peaceful use of nuclear energy. Both sides confirmed their commitment to this collaboration, and agreed to conduct a joint sample analysis on a low-enriched nuclear fuel pellet reference material.

1.2 Points of Contact

POCs Argentina:
TBD

POCs U.S.:

- Project lead: Ms. Kaitlin Oujo
  Foreign Affairs Specialist
  Office of Nuclear Smuggling Detection & Deterrence
  National Nuclear Security Administration (U.S. DOE/NNSA/NSDD)
  kaitlin.oujo@nnsa.doe.gov
- Scientific POC: Dr. Ruth Kips
  Deputy Associate Program Leader International Nuclear Forensics
  Lawrence Livermore National Laboratory
  kips1@lllnl.gov

2 Project Description

2.1 Material for Comparative Sample Analysis

The recent workshop on analytical plan development provided context and background for the next step in this engagement, i.e. a comparative sample analysis on CRM 125-A. This is a commercially available certified low-enriched uranium oxide fuel pellet material from New Brunswick National Laboratory (NBL) (see certificate in Annex 1).

Each participating laboratory/network of laboratories will start the sample analysis from an intact CRM 125-A pellet.

2.2 Participating Laboratories

The participating laboratories on the Argentina side include:

TBD

The participating laboratories on the U.S. side include:

- Lawrence Livermore National Laboratory (LLNL), Livermore, California
- Los Alamos National Laboratory (LANL), Los Alamos, New Mexico

2.3 Project Tasks and Objectives

The tasks and objectives for the Argentina-NSDD Comparative Sample Analysis on the CRM 125-A UO_2 fuel pellet are described below:

1. Identification of participating laboratories and development of analytical plan applied to the joint sample analysis.
2. Nuclear forensic analysis of pellet material (intact CRM 125-A UO_2 fuel pellet).
3. Joint Argentina/LLNL/LANL meeting to discuss analytical results and share best practices in terms of sample analysis and data reporting.

2.4 Proposed Techniques for Analytical Plan on NBL CRM 125-A

Analytical Technique	Laboratory		Type of data
	Argentina	LLNL/ LANL	
Visual Inspection, photography	x	x	Macroscopic features, color
Weighing	x	x	Sample mass
Optical microscopy	x	x	Grain size, morphology
Dosimetry	x	x	Dose rate, gamma, beta and alpha activity
Pycnometry	x	x	Density
Scanning Electron Microscopy (SEM)	x	x	Grain size, morphology
Transmission Electron Microscopy (TEM)	x	-	Grain size, morphology
Autoradiography		x	Homogeneity in activity
Energy/wavelength-dispersive X-ray Analysis	x	x	Elemental composition
Gamma-spectrometry	x	x	Uranium isotopic ratios
Alpha-spectroscopy	x	x	Specific activity of $^{239+240}$Pu and ^{238}Pu
X-ray Fluorescence (XRF)	x	x	Semi-quantitative major element composition
X-ray Diffraction (XRD)	x	x	Crystallography/composition
Davies-Gray Titration	x	x	Uranium concentration
Uranium concentration by ID Mass Spectrometry	x	x	Uranium concentration
Elemental composition by ICP-MS	x	x	Major and trace element concentrations
Elemental composition by ICP-OES	x	-	Major and trace element concentrations
Uranium isotopic composition by ICP-MS and/or TIMS	x	x	Uranium isotopic ratios
Radiochronometry		x	Date since last chemical purification

2.5 Reporting of Results

With reference to techniques listed above, each institute is encouraged to provide the following information in addition to the analytical data:

- Instrument type that was used for the measurements
- Type of data obtained from the instrument
- Sample preparation process
- Analysis timeline
- Reference materials and standards that were used
- Uncertainty on the results and the way that uncertainty was obtained
- Calibration practices and standard operating procedures

3 Project Timeline

Proposed project timeline (tentative - subject to change):

- December 2017- March 2018: CRM 125-A UO_2 pellet analysis
- April 2018: Results compilation
- May 2018: Data comparison meeting
- June-July 2018: Preparation of comparative sample analysis report

4 ANNEX 1: NBL CRM 125-A CERTIFICATE OF ANALYSIS

New Brunswick Laboratory
U.S. Department of Energy

Certificate of Analysis
CRM 125-A
Uranium (UO_2) Pellet Assay, Isotopic, and Radiochronometric Standard

Amount Content :	**0.88129**	**g U•g^{-1} pellet**		
Uncertainty:	**0.00014**	**g U•g^{-1} pellet**		
	$n(^{234}U)/n(^{238}U)$	$n(^{235}U)/n(^{238}U)$	$n(^{236}U)/n(^{238}U)$	
Isotope-Amount Ratio:	**0.00039130**	**0.042301**	**0.0000040754**	
Uncertainty:	**0.00000038**	**0.000025**	**0.0000000047**	
	$n(^{234}U)/n(U)$	$n(^{235}U)/n(U)$	$n(^{236}U)/n(U)$	$n(^{238}U)/n(U)$
Isotope-Amount Fraction (•100):	**0.037528**	**4.0569**	**0.00039085**	**95.9052**
Uncertainty:	**0.000037**	**0.0023**	**0.00000045**	**0.0023**
	$m(^{234}U)/m(U)$	$m(^{235}U)/m(U)$	$m(^{236}U)/m(U)$	$m(^{238}U)/m(U)$
Isotope Mass Fraction (•100):	**0.036915**	**4.0077**	**0.00038776**	**95.9550**
Uncertainty:	**0.000036**	**0.0023**	**0.00000045**	**0.0023**

Molar Mass:	**237.927291**	**g•mol^{-1}**	**Model Purification Date:**	**August 18, 1994**
Uncertainty:	**0.000071**	**g•mol^{-1}**	**Uncertainty:**	**116 days**

Notes:

CRM 125-A is a radioactive material and should be handled and stored under proper radiologically-controlled conditions at all times.

Certified Reference Material 125-A (CRM 125-A) is a uranium amount content, isotope-amount ratio, and radiochromometric standard intended for use in calibration of and/or quality control for analysis of uranium in fabricated fuel form. Each unit of CRM 125-A consists of one enriched uranium dioxide (UO_2) pellet with a mass of approximately 5.4 grams.

Reported numerical uncertainties for certified values are expressed as expanded uncertainties ($U = k \cdot u_c$) at the 95% level of confidence, where the expanded uncertainty (U) is the product of the combined standard uncertainty (u_c) and a coverage factor (k). The last figure in the reported values and their uncertainties is provided for information purposes and is not intended to convey a significant degree of reliability. The isotope-amount and mass fraction values and uncertainties are provided primarily for information purposes. To assure proper uncertainty propagation, it is recommended that isotope-amount ratios and associated uncertainties be used for calculations incorporating CRM 125-A values.

CRM 125-A units do not have an expiration date. To maintain the integrity of an unused CRM unit, it should remain in the original packaging and should be stored in a dry, temperature-controlled location.

(Revision of Certificate dated December 1, 1997)
Steven Bakhtiar, Director
March 4, 2013

Page 1 of 3

New Brunswick Laboratory
Argonne, Illinois
www.nbl.doe.gov

Certification and/or verification measurements for uranium amount content, isotope-amount ratios, and model purification date were performed on a random sampling of UO_2 pellets. All analyses were performed on pellets that were dissolved in their entirety. Accordingly, the material homogeneity for the attribute values is not certified for samples smaller than a single UO_2 pellet.

Note that small quantities of refractory particulates have been observed following nitric acid-only sample dissolution but do not have a discernible effect on the measurement of values cited in this certificate. The total metal impurity content is estimated to be less than 80 $\mu g \cdot g\ pellet^{-1}$ as determined by optical emission spectrometry. This impurity content value is provided for information only and is not certified. Therefore, if this material is analyzed by gravimetry, it is the responsibility of the user to determine and subtract impurity content, as necessary.

Description:

Uranium amount content for CRM 125-A was originally determined in 1997 by the NBL High Precision Titrimetric method using CRM 99 Potassium Dichromate Oxidimetric Standard as the titrant. The CRM 112-A Uranium Metal Assay and Isotopic Standard was used as a control to verify performance of the measurement system. In addition, gravimetric analyses were performed to verify that pellet-to-pellet inhomogeneity was negligible. Traceability of the measurements is primarily established by direct determination of uranium amount content based on the titration of uranium using CRM 99 Potassium Dichromate Oxidimetric Standard.

In 2011 to 2012, a detailed thermal ionization mass spectrometry measurement campaign was performed on the CRM 125-A to refine uranium isotope-amount ratios and uncertainties. Mass discrimination calibrations were performed on a sample-turret basis using multiple measurements of NBL CRM U030-A Uranium Isotopic Standard. Analyses of CRM U045 Uranium Isotopic Standard were performed to verify that mass spectrometric measurements were in control. Traceability of the isotope-amount ratio measurements for CRM 125-A is primarily established by calibration of the mass spectrometer using measurements of CRM U030-A Uranium Isotopic Standard that was originally provided by the National Bureau of Standards (now known as the National Institute of Standards and Technology) as SRM U030a Uranium Isotopic Standard.

In 2011 to 2012, a detailed study was performed to determine the model U purification date for the CRM 125-A pellets. The certified purification date is a derived value based on the ^{234}U-^{230}Th isotope parent daughter system (Equation 1) and is consistent with independent measurements using the ^{235}U-^{231}Pa isotope parent daughter system. The certified value represents results for combined measurements from 3 laboratories: Argonne National Laboratory facility (Bldg 203), the ACL lab at Argonne National Laboratory (Bldg 205), and New Brunswick Laboratory. The variables necessary for the derived value include ^{234}U content (N_{234U}), ^{230}Th content (N_{230Th}), and the decay constants of both isotopes (λ_{234U}, λ_{230Th}). The ^{234}U content was derived from the certified amount content and isotope mass fractions. The ^{230}Th content was determined by isotope dilution α spectrometry using ^{229}Th Radioactivity Standard, SRM 4328C, provided by the National Institute of Standards and Technology. It is the direct comparison of measured activity between ^{230}Th in the sample and the SRM 4328C ^{229}Th added to the sample that provides traceability for the measurements used to determine the certified value. The model purification date, based on the combined measurements, is provided as a fixed certified value for this material because the ^{230}Th content of CRM 125-A changes continuously due to in-growth. For information purposes, the composite value for ^{230}Th content, as of January 2012, is 7.0×10^{-11} $mols \cdot g\ pellet^{-1}$. The decay constants used for the purification date calculations are $\lambda_{230Th} = (9.193 \times 10^{-6} \pm 0.073 \times 10^{-6}) \cdot year^{-1}$ and $\lambda_{234U} = (2.823 \times 10^{-6} \pm 0.014 \times 10^{-6}) \cdot year^{-1}$ (calculated from half-lives provided in the NNDC Nuclear Wallet Card Database June 1, 2012).

Equation 1: $$Model\ Purification\ Date = t_{separation} - \frac{\ln\left[1-\left(\frac{\lambda_{230Th}-\lambda_{234U}}{\lambda_{234U}}\right)\times\left(\frac{N_{230Th}}{N_{234U}}\right)\right]}{(\lambda_{234U}-\lambda_{230Th})}$$

$t_{separation}$ is the date of Th separation for the analysis samples.

Measurement Uncertainty:

Uncertainties were determined according to the protocols outlined in JCGM 100:2008 *Guide to the Expression of Uncertainty in Measurement*. The combined standard uncertainties for certified values consist of Type A and Type B components. The Type A uncertainty component for amount content is derived from the standard deviation of the titrations. The Type B component is the combined standard uncertainty of the CRM 99 oxidimetric standard. The Type A components for isotope-amount ratios are derived from standard deviations associated with isotopic ratios measured for the samples and the $n(^{235}U)/n(^{238}U)$ ratio of NBL CRM U030-A. Type B components are based on the combined standard uncertainties for the certificate-derived $n(^{235}U)/n(^{238}U)$ ratio of CRM U030-A and components to account for additional sources of uncertainty associated with background corrections and analytical biases. Isotope mass fractions incorporate an additional Type B component associated with the uncertainty of the atomic mass for the U isotopes. The Type A uncertainty component for the Model Purification Date is derived from the standard deviation of the replicate age determinations. Type B Components include SRM 4328C certificate uncertainty, C125-A U amount content and isotope mass fraction uncertainties, U and Th half-life uncertainties, and Th activity data correction factors. The coverage factor (k) for each expanded uncertainty is the Student's t-factor necessary to provide a 95% level of confidence ($k \approx 2$ for all values cited in this certificate). A more detailed explanation of measurement uncertainty can be obtained upon request from NBL.

Project Support:

Characterization analyses for revised isotope-amount ratio measurements and the model purification date determination were funded by the Department of Homeland Security, National Technical Nuclear Forensic Center (NTNFC) under Inter-Agency Agreement HSHQDC-10-X-00135.