ORNL/LTR-2015/502

# End-of-Year Report: Qualification of Very Pure $^{233}U$ for Use in Uranium Analyses




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OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE US DEPARTMENT OF ENERGY

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# Qualification of Very Pure $^{233}U$ for Use in Uranium Analyses
# Project Number: OR13-U233029-PD3SA

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## ACRONYMS AND ABBREVIATIONS

| | |
|---|---|
| ADU | ammonium diuranate |
| CRM | certified reference material |
| DOE | U.S. Department of Energy |
| FY | fiscal year |
| LANL | Los Alamos National Laboratory |
| NM | nuclear material |
| ORNL | Oak Ridge National Laboratory |
| REDC | Radiochemical Engineering Development Center |
| HFIR | High Flux Isotope Reactor |

# QUALIFICATION OF VERY PURE $^{233}$U FOR USE IN URANIUM ANALYSES

**Project Number OR13-U233029-PD3SA**

## 1. INTRODUCTION

Pure $^{233}$U certified reference material (CRM) is an essential material used in the most precise method for determining the uranium element and isotopic concentrations in samples bearing only trace uranium concentrations—which is important particularly for forensic and environmental samples. This report delineates the progress made during Fiscal Year (FY) 2015 in qualifying very pure $^{233}$U for eventual use in uranium analysis. Ultimately, qualified material will be processed as needed to replenish depleting supplies of $^{233}$U CRM used in uranium analysis, not only on forensic and environmental samples, but on safeguards samples as well.

## 2. QUALIFICATION PROCESS

The steps in qualifying high isotopic purity $^{233}$U are:

A. Redirect the material from the downblend stream. This involves receiving candidate CRM items from the repository [co-located with Oak Ridge National Laboratory (ORNL)] where plans are being made for downblend and disposal of all $^{233}$U in storage there. [All but two items have been redirected from the downblend stream; the two remaining items (99.5% isotopic pure $^{233}$U) comprise ~45% of the $^{233}$U slated for preservation.] Shown in Fig. 1 is a shipping drum containing high-purity $^{233}$U being removed from the repository (left) for staging (temporary storage) at an ORNL facility (right) to await qualification processing.

**Fig. 1. Shipping drum containing high purity $^{233}$U being removed from the repository (left image) and being received at an ORNL staging (temporary storage) facility (right image).**

B. Confirm the isotopic purity of redirected $^{233}$U materials to ensure their fitness for intended use in later certification processing and, ultimately, as CRM. To confirm the isotopic purity, the following actions must be performed for each distinct item:

a. Unpack – Figure 2 shows solid materials as the container was unpacked (left) and, in this case, segregated since solids did not appear (right) to be of a common source [i.e., different textures possibly indicating mixed materials, plus debris from handling (e.g., brush hairs, paper or plastic fragments, etc.)].

**Fig. 2. Unpacking solid materials. Image at right shows some debris warranting segregation (brown brush hair, rusted pieces, white paper flecks, etc.).**

b. Dissolve – Figure 3 shows image**s** of oxides being dissolved (left) and completely dissolved uranyl nitrate solution (right). Materials not considered stable typically are dissolved before stabilization. [See 2.B.c. Sample for cases not requiring dissolution.]

**Fig. 3. High purity $^{233}$U being dissolved (left) and completely dissolved (right). [A magnetic stirring bar can be seen in the bottom of flask in both images.]**

c. Sample – For items that have been dissolved, sampling involves acquiring triplicate samples of the liquor. Certain solids can be sampled without first dissolving the bulk material:

   i. Homogeneous oxides must be free-flowing and appear homogeneous (i.e., no obvious color or morphology variations) and amenable to *representative* sampling. Achieving homogeneity for solid powders can be very difficult – including milling and blending for a period established by experimental determination (specific to the milled material and blending equipment itself) – and should be avoided (or not relied upon), if possible, by sampling in a liquid form.

   ii. Metal pieces can be pickled to remove the thin layer of oxide (a passivation layer) formed on the surface. However, the passivation layer may include some minor amounts of atmospheric uranium, which are NOT representative of the bulk metal. To avoid being misled by atmospheric uranium degrading the oxide layer's purity, interior portions of the metal also are sampled by cutting into the piece (or by dissolving a few pellets for certain items) during the sampling process.

   However, items that are not dissolved still must meet the packaging and storage standard [Ref. 1] which involves either meeting a specific surface area criterion (for metals; small metal pieces, foils and wires are not considered to be stable forms) or meeting a stabilization criterion (for all other material forms not considered engineered materials; e.g., clad fuels).

d. Analyze – Samples are analyzed for total uranium content, uranium isotopics (including $^{232}U$), and the presence of other actinides which can interfere with eventual certification processing.

C. Prepare qualified, pure $^{233}U$ items for compliant storage [Ref. 1] (either at ORNL, or the Nuclear Material (NM) Archive located at the Los Alamos National Laboratory (LANL). As part of preparing the material for storage, the following actions must be performed:

   a. Stabilize – Figure 4 shows images of uranium precipitated as ammonium diuranate, filtered and calcined to an oxide. For compliant storage, oxides must be calcined at >750°C and verified to ensure that the volatiles content is less than 0.5 wt%.

      Metals are considered stable if they have a specific surface area of less than 0.005 $m^2/g$ (larger than 8 mesh) and are free of non-adherent oxides, liquids and organic materials; otherwise, they must be converted to a stable oxide—which, to facilitate representative sampling, typically involves dissolution followed by precipitation and calcination to a stable oxide.

   b. Re-pack – Stable materials must be packed in a minimum of two individually sealed, nested containers. The storage standard [Ref. 1] provides very prescriptive guidance on this. Figure 5 shows an expanded view of the nested configuration before welding.

**Fig. 4. High-purity $^{233}$U precipitated as ammonium diuranate (left) and filtered (upper right). Lower right image shows calcined oxide, ready for loading into a bored-plug container (standing next to the oxide, with a funnel in place for filling).**

**Fig. 5. Expanded view of container used for long-term storage**.

c. Store – The pure $^{233}$U materials being qualified and preserved by this project have been accepted for storage at the NM Archive at LANL (NMIP Sample Identification Numbers NMIP-11-019 through NMIP-11-036). [Qualified items can be staged at ORNL until LANL is ready to receive them.]

Other considerations in the qualification process include:

- Material sequencing in a manner that reduces the chance of less pure items contaminating more pure items
- Limiting batch sizes to ensure that safety, safeguards and transportation limits are not exceeded for any activity or material movement
- Arranging extra actions (e.g., removing fixtures used for repository handling) and taking special precautions while opening items (e.g., in an inert or nitrogen atmosphere)

## 3. $^{233}$U QUALIFICATION PROGRESS IN FISCAL YEAR 2015

Progress was made in the following areas related to qualifying high-purity $^{233}$U:

**Qualified Item TAR-LB1.** This item was qualified this year and found to be 99.7659%-pure $^{233}$U (with a 0.0012% standard deviation); this confirms its recorded purity of 99.76% $^{233}$U. While still in liquid form, TAR-LB1 also was processed to recover $^{229}$Th (performed for, and funded by, another program), and now is being stabilized and packaged for storage in compliance with the applicable standard (DOE-STD-3028-2000). This material was stabilized for storage in compliance with the standard and packaged in a manner consistent with the applicable standard (*Criteria for Packaging and Storing Uranium-233-Bearing Materials*, DOE-STD-3028-2000, July 2000).

A second item of this batch had a documentation error requiring resolution with the U.S. Department of Energy (DOE) Site Office. Since that issue was resolved after qualification of TAR-LB1 was complete, this second item was set aside temporarily to be qualified when other like materials are handled. In the interim, a slightly purer batch of $^{233}$U will be qualified. This purer batch had been passed over since items comprising the batch included fluorides, and the flowsheet for qualifying them had not yet been identified, adapted and tested when the operating window opened for handling the next batch. As a result of this opening, TAR-LB1 was moved up in the sequence. [Recognizing that TAR-LB1 was slightly lower in isotopic purity than the passed-over batch, special precautions are being taken (box cleanout, survey and contamination analysis for purity) to ensure that the integrity of the passed-over batch is not compromised.]

**Adapted a Flowsheet for Dissolving $^{233}UF_4$.** A flowsheet was identified, adapted and tested successfully for dissolving fluoride powders ($UF_4$) in the next batch of $^{233}$U (99.9% pure). From limited available literature, it has been shown that, at relatively low temperatures (i.e., heated, but well below the boiling point), a strongly oxidizing acid eventually will dissolve $UF_4$—without evolving copious amounts of fluoride gasses (which will attack stainless steel comprising most of the off-gas system ductwork). [Ref. 2]

Basically, the reaction is a straightforward metathesis of $UF_4$ and $HNO_3$, during which the uranium (at valence IV) is oxidized (to valence VI) resulting in a clear, bright yellow, uranyl nitrate [$UO_2(NO_3)_2$] hexahydrate (UNH) solution. The reaction was confirmed by gently heating (at 60°C) a loosely capped Teflon vessel containing 0.5 g of $UF_4$ and ~20× (by mass) 8N $HNO_3$ (optima grade). [As with any heated acid dissolution containing fluorides, there exists the possibility that some HF will evaporate; however, with a condensing-vessel system heated only to a slightly elevated temperature, the acid vapors will readily condense and be refluxed back into the dissolver solution.] Essentially complete (>99%) dissolution of the $UF_4$ was realized in this 10 mL test case after about a day and a half of heating (i.e., more than 36 h).

The solution then was filtered to remove any insoluble species (which can be treated further, if needed). The filtrate was precipitated with ammonium hydroxide ($NH_4OH$), a routine uranium precipitation process, yielding ammonium diuranate [ADU; $(NH_4)2U_2O_7$; a bright yellow paste] which can be calcined to a stable oxide.

Essentially all of the fluorides will be neutralized to a highly soluble ammonium fluoride ($NH_4F$) in the precipitation process. The ammonium fluoride will remain with the ammonium nitrate in the aqueous solution; any trace ammonium fluoride (as with trace ammonium nitrate) remaining in the ADU solids, will be removed upon calcination.

$UF_4$ dissolution will be a longer process and, since it cannot be conducted overnight (without attending it), it likely will require several day-shifts of heating. However, the reaction is clean with no new reagents introduced into the uranium that are not already part of the qualification flowsheet. Additionally, the process can be confined to the dedicated $^{233}U$ gloveboxes, thus reducing the potential for introducing ubiquitous uranium contamination.

**Performed More Complete Risk Evaluation.** An observation resulting from the 2014 Independent Project Review called for performing a more complete evaluation of risks that incorporates lessons learned from processing the first batch of ultra-pure $^{233}U$ material. Exploiting the period of suspended operations, $^{233}U$ handling personnel and project management conducted a risk evaluation. This evaluation identified several vulnerabilities for which preventive actions have been implemented.

The evaluation focused on activities involved in directly handling high-purity $^{233}U$ and addressed events that were considered credible (ignoring beyond-credible events which typically are considered in safety analyses for nuclear facilities). Twenty-eight individual actions were evaluated, for which 55 potential consequences were identified.

Of the 55 potential consequences, twelve represented new scenarios (beyond those identified in initial job planning) which had to be evaluated. All 12 potentially impact material quality and can be grouped in one of two potential consequences, each occurring several times in the process:

1. Loss of most material due to spillage or broken laboratory glassware (five of the consequences, all posing a high risk to material quality).

2. Contamination of material (seven of the consequences, posing medium or low risks to material quality).

Measures to mitigate consequences of the new scenarios include:

- Limiting batch sizes to avoid placing an entire purity-group of $^{233}U$ materials at risk at any given time.

- Placing trays under glass flasks containing batches of material where it is practical to do so. (Some areas of the glove boxes are too cluttered with equipment to accommodate tray placement.)

- Scraping coatings off interior glovebox surfaces as they come loose. (One source of previously unrecognized contamination is a strippable coating—supposedly more environmentally friendly than those used for similar applications in the past—that began peeling prematurely. The coating was applied to the glove box interior surfaces to facilitate decontamination as part of the effort to limit/prevent cross-contamination between batches.)

- Covering containers when material is substantially exposed to the threat of debris falling into them.

Additionally, the potential loss of key staff on the project was evaluated and found to pose a high risk to the project. The identification of backup personnel and their integration into the project has been implemented and was considered sufficient mitigation of the risk posed by this potential loss of staff. (A consequence of this risk has been realized as the project's principal investigator

will be leaving the project for a temporary technical advisor position in the Office of Nonproliferation and Arms Control.)

A write-up of the evaluation process was compiled, and the results were transmitted to the Program Manager at DOE Headquarters in December.

**Qualified a Compact, Welded-Container.** A compact, welded-container configuration was qualified for compliance with the $^{233}$U storage standard (DOE STD-3028-2000). Test containers with simulated loads passed all drop and pressure tests (for which biennial container qualification was coming due) to fully comply with storage standard requirements. The compact configuration is more optimal for utilizing storage space than the earlier, larger-diameter version. [It is notable that drop and leak tests were conducted using equipment that was fabricated or procured in fiscal year (FY) 2012, before the qualification project commenced (i.e., when the $^{233}$U qualification capability was being established with funding from the predecessor of the Office of Nonproliferation and Arms Control).]

**$^{233}$U Coordination and Planning.** Much of the coordination and planning effort this fiscal year focused on establishing additional, new areas for staging $^{233}$U. Due to efforts during recent past decades at ORNL, the footprint of nuclear and radiological facilities has undergone a transition to a more optimal configuration than was in place in earlier years. This has resulted in fewer such facilities, a ramification of which is that ORNL has a reduced capacity for storing nuclear materials. This reduces the ability of the project to stage (i.e., temporarily store) $^{233}$U which, in turn, impacts the readiness to anticipate and prepare for upcoming qualification activities. (Indeed, two of the largest high-purity $^{233}$U items remain in the repository solely because of this reduced capacity.)

To address this concern and to alleviate the staging bottleneck, an existing excess modular vault has been acquired for use by the project and has been activated as a storage area. Efforts continue to upgrade this vault's service category so that it can handle larger amounts of nuclear material (which is necessary for receiving the remaining items from the repository) without impacting other operations around ORNL.

## 4. OTHER OPERATING FACTORS IN FISCAL YEAR 2015

The fiscal year started with the high-purity $^{233}$U handling laboratory shut down while a hood in the laboratory was being replaced (funded by another project). Although the hood's replacement was completed early in the fiscal year (mid-October), higher-priority work occupied the lead technician for $^{233}$U qualification. A backup chemist was being trained at the time, but an NM accountancy issue in the facility [distracting the lead technician who also serves as the Materials Balance Area (MBA) representative responsible for NM accountancy] interfered with the training's completion.

During the second quarter, in-laboratory work and training resumed although, again, higher-priority work occupied the lead technician intermittently for most of the quarter as a backlog of nuclear projects had to be addressed to minimize impacts on major milestones. $^{233}$U qualification work relies on analytical laboratory personnel at Radiochemical Engineering Development Center/High Flux Isotope Reactor complex (REDC/HFIR). (From a facility operations perspective, projects impacting the main REDC mission—isotope production—were designated as the highest priority. Direct-handling of $^{233}$U is conducted in the REDC and, hence, competes with this work.)

**In August, training of the chemist was completed, and he is being committed to provide uninterrupted support to the $^{233}$U qualification project.**

It is notable that the modification during which a hood was replaced (causing the extended shutdown of the $^{233}$U handling laboratory) accommodates a new capability in that laboratory which should facilitate $^{233}$U qualifications. The new hood has a new, inductively coupled-plasma – mass spectrometry (ICP-MS) unit which will save the time, delay and inconvenience of transporting high-purity $^{233}$U samples to the main mass spectrometry laboratory located in a different area of ORNL.

## 5. PATH FORWARD

With a dedicated analytical chemist to conduct high-purity 233U qualifications—without distractions—the anticipated qualification pace is expected to be one batch every three months. Batches are identified below with their designated items (which are subject to change). Batch letters reflect relative purity, with 'B' representing the 99.8%-pure and 99.9%-pure material, and 'C' reflecting the 99.5%-pure material. The following delineates individual batches for future processing:

- B2 – 99.9%-pure items (KZA-G1B3 and RCP-16) totaling 80 g $^{233}$U
- B3 – the balance of 99.8%-pure items [JSG-3, CZD-G(CY)#1, KZA-G1B4, SNM-9514 and SNM-9514-1] totaling 75 g $^{233}$U
- C1 – several 99.5%-pure items (AUA-94B, JSG-2, OX-343, SNM-4031, SR2R and SR2R-1) totaling 49 g $^{233}$U
- C2 – Items CZD-G(CZ)#4 and CZD-G(CZ)#8 (packed together in one can) totaling 91 g $^{233}$U
- C3 – Item KZA-G1B2 containing 158 g
- C4 – Item PZA-126 containing 282 g $^{233}$U

It is notable that the last two batches (i.e., Items KZA-G1B2 and PZA-126) have not yet been received from the repository. With its current staging capabilities, ORNL cannot receive the items until much of the high-purity materials on hand are qualified and shipped to the NM archive at LANL, or until additional staging capacity can be established. As funding allows, ORNL will receive and qualify one or both of these last two items for preservation.

## 6. FY 2015 COSTS ($K; as of 09/22/2015)

| **Total FY 2015 Budget Authority** | **659** |
|---|---|
| TAR-LB1 Qualification | 123 |
| $UF_4$ Flowsheet Adaptation | 15 |
| Risk Evaluation | 39 |
| Can Compliance Testing | 63 |
| $^{233}$U Coordination and Planning | 88 |
| Travel | 41 |
| **Remaining FY 2015 Budget Authority (est.)** | **290** |

## 7. PRESENTATIONS AND PUBLICATIONS

A presentation was made on October 28th by the Principal Investigator at the Radiobioassay and Radiochemical Measurements Conference, sponsored by the Health Physics Society, held in Knoxville, Tennessee. The presentation was titled "*Need for U-233 Reference Materials*."

A poster presentation entitled *Qualification of Pure U-233 for Uranium Analyses* was made on March 18th at the WMS Program Review Meeting held at the Lawrence Livermore National Laboratory.

A workshop dedicated to discussions on "Preserving High-Purity Uranium-233" was held on April 12th at the Conference on Methods and Application of Radioanalytical Chemistry held in Kailua-Kona, Hawaii. The workshop was co-chaired by the Principal Investigator, Alan Krichinsky, and the project's Analytical Coordinator, Joe Giaquinto. A report on the results of the workshop, entitled "*Workshop on Preserving High Purity Uranium-233*" is being published as part of the conference proceedings (not yet released).

## 8. REFERENCES


1. DOE Standard Criteria for Packaging and Storing Uarnium-233-Bearing Materials, U.S. Department of Energy, DOE-STD-3028-2000, July 2000.
2. The Chemistry of the Actinide and Transactinide Elements, Springer, Dordrecht, NL, Chapter 8, Page 485, 2008.