Proceedings of the INMM & ESARDA Joint Virtual Annual Meeting
August 23-26 & August 30-September 1, 2021

Preparation of Specimens and Samples for the US National Nuclear Materials Archive

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Abstract

Physical specimens of US Department of Energy–origin nuclear materials obtained from key points in the fuel cycle are being retained by the National Nuclear Materials Archive (NNMA) and are being sampled, stabilized, and packaged for archival storage. Samples acquired from each specimen are being analyzed for baseline characterizations at two or more analytical laboratories qualified to perform forensic analyses for the archive. This paper describes the activities involved in the preparation of materials at Oak Ridge National Laboratory (ORNL) for archival storage. These activities used glove box laboratories and other resources of the Radiochemical Engineering Development Center, a US Department of Energy Office of Science research facility operated by ORNL. The NNMA is led and managed by the Office of Nuclear Forensics, located in the Counterterrorism and Counterproliferation Office of the National Nuclear Security Administration.

Introduction

Items of interest to the NNMA, such as ^{233}U and ^{237}Np, for characterization are being packaged for archival storage at ORNL. Uranium-233 specimens were produced at the Hanford and Savannah River Sites in the 1960s, primarily for the Light Water Breeder Reactor Demonstration Program. Solid forms of ^{233}U from the site(s) were precipitated to ammonium diuranate and calcined to an oxide or converted to oxide by thermal denitration. These materials were transferred to ORNL where most of the ^{233}U was prepared as a ceramic-grade oxide to feed fuel pellet–making at the Bettis Atomic Power Laboratory. Solid forms of ^{233}U prepared at the production sites are valued as specimens for their production provenance because they were recovered during reprocessing of irradiated thorium targets and converted to oxides. Other ^{233}U specimens are valued for their very high purity of the ^{233}U isotope, rather than their chemical or physical form.

Neptunium-237 specimens resulted from previous chemical processing in the H-Canyon Facility at the Savannah River Site during the 1970s and 1980s. The neptunium was retained as a nitrate solution until 2003, when the decision was made to stabilize the neptunium to an oxide in the HB-Line Facility in support of future ^{238}Pu production. After purifying and concentrating the neptunium nitrate by anion exchange, stabilization involved precipitation with oxalic acid, filtration of the neptunium oxalate, and calcination at >635°C for at least 3 hours to form neptunium oxide (Watkins, Hensel, and Jordan 2009). The neptunium oxide product cans were shipped to Idaho National Laboratory for storage until needed for ^{238}Pu production at ORNL for NASA space missions.

Sample Acquisition for Characterization Analysis

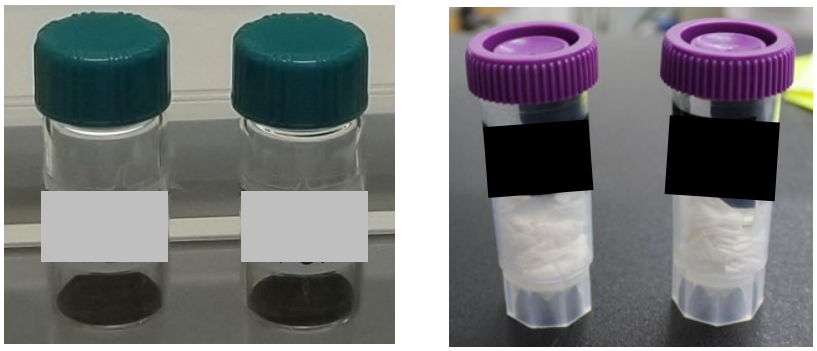
Sample acquisition for newly stabilized material is different from that for a production specimen with chemical or physical characteristics that require preservation. The following are key steps of a protocol for sampling stabilized powdered or agglomerated compounds (e.g., oxides) for the NNMA characterization:

1. Granulate any solid specimen masses to an extent that the bulk material *appears* to be a homogeneous powder (i.e., solid particles are observed to have consistent texture and size throughout the bulk material).

2. Mix the specimen by stirring in a manner that ensures particles of different sizes and colors from essentially all portions of the bulk material *appear* evenly distributed.

3. Acquire sample aliquots that, together, will make up the sample amount from multiple (preferably three or more) disparate regions of the powder. Aliquots may be acquired using a special sampling tool (e.g., one which can sample regions below the material's exposed surface), or they may be acquired while exposing below-surface volumes by rotating the container when it is tilted. Aliquots are combined in a precleaned glass vial with a plastic screw-cap closure. Samples acquired by this latter technique are shown in Figure 1. To an undefined extent, sampling disparate regions of an apparently well-mixed, bulk material is intended to compensate for a less-than-optimal and otherwise-unqualified sampling process and to result in a more representative sample than would be acquired by simply "grabbing" a sample from the bulk material.

Figure 1 shows (*left*) a pair of neptunium oxide samples in glass vials ready for bag out and (*right*) a pair of ^{233}U oxide samples after bag out and overpacking in an outer plastic vial.



A pair of neptunium-237 oxide samples in glass vials ready for bag out.

A pair of uranium-233 oxide samples overpacked in a plastic vial after bag out.

Figure 1. Samples of NNMA specimens.

Sampling specimens with significant chemical or physical characteristics that vary in complexity depends mostly on the form of material being preserved. Sampling may be performed in an inert atmosphere to avoid alteration of both the chemical and physical attributes (especially for some metals that are pyrophoric). Alternatively, sampling compounds may be performed in an ambient atmosphere if no special measures were taken previously to isolate the material from ambient conditions. The approaches for sampling compound and metal specimens for NNMA characterization are as follows:

- Compounds include halogenic species but most are oxides. They are not pyrophoric under ambient conditions, which is the case for several metals, but they can undergo slower transformations (such as hydration), which can lead to substantial expansion and compromised confinement. Therefore, the environment in which they are handled may warrant special considerations to retain chemical and physical characteristics.
    - For powders, multiple aliquots are acquired as described above for newly stabilized specimens. Although no attempt is made to ensure consistent sizes throughout the

specimen, judgment is needed to ensure that aliquots include disparate sizes representing the bulk material or are used to form separate samples reflecting different sizes (for separate analysis).
    - For many pieces ("chunks") of various-sized compounds (e.g., oxides), many smaller pieces can be broken off and collected. Much judgment goes into sampling many small pieces because individual pieces may appear different in color and texture, and a newly exposed surface may appear different compared to an older outer surface.
    - For monolithic compounds (e.g., blocks of triuranium octoxide [U_3O_8] resulting from in situ denitration), simply drilling into the mass provides debris for collection as samples.
- Several actinide metals are pyrophoric, requiring use of precautionary practices (e.g., inert atmosphere, lubricating coolant) to avoid rapid oxidation during sampling.
    - For many small metal pieces, small portions may be broken off several of the metal pieces, similar to sampling pieces of compounds. Samples for most metals will have surface oxidation that will have altered the specimen's surface chemical and physical characteristics. Similarly, metal that is newly exposed by breaking off pieces will rapidly oxidize as well.
    - For a solid metal or alloyed specimen, samples are acquired by drilling into the mass, similar to sampling monolithic compounds but with the added precautions noted previously.

Collecting sample aliquots from multiple pieces or from multiple points in solid masses will help quantify and minimize uncertainties of sampling and their characterizations. Precautions and specific steps for sampling specimens falling into any of the above material forms—for which physical and chemical conditions are being preserved—will be detailed in a material-specific instruction in preparation for the sampling evolution.

Preparing Specimen for Storage

After a specimen is sampled for analysis, it is prepared for storage. The forensic value of a specimen (i.e., its unique set of characteristics) must be maintained in storage. Maintaining specimen integrity involves preparations to protect the specimen from degradation resulting from conditions within the storage container and from the storage facility environment. The storage facility is presumed to be robust (i.e., designed to protect the environment and workers from the stored material and protects the specimen from impacts caused by a failure in the storage facility environment).

Specimen preparations for storage follow one of two distinct paths: preparations to stabilize the material for safe storage or preparations to preserve chemical and physical characteristics over the period of storage. The path chosen depends on the significance of the specimen's provenance. Items with significant, established provenance are packaged in a manner that preserves their characteristics. For example, they may be canned in a dry or inert atmosphere, if warranted. Items with less-significant provenance (e.g., their value relates more to their purities than their production histories and product characteristics) are stabilized *before* they are canned—typically in an ambient atmosphere. The timing for acquiring specimen samples in each path ensures that the samples (and their baseline characterizations) reflect the stored material.

If the chemical or physical form is not a crucial forensic attribute, a specimen may be converted to a stable chemical form (typically, an oxide) to ensure safe storage in air. Typically, for these cases, specimens to be included in the NNMA are being drawn from items belonging to (and undergoing processing for) another program. Stabilization includes calcining the specimen at conditions that ensure

low volatile (moisture and organic) contents. Moisture and organic materials are driven off at calcination conditions (nominally ranging from about 400°C–1,100°C), leaving only volatile residues that, at low concentrations, will not result in a dangerous level of flammable by-products produced by radiolytic degradation. For example, U_3O_8 specimens stabilized at ORNL typically are calcined at >800°C, and volatile contents are confirmed to contain <0.5% moisture by loss-on-ignition measurements at a higher (by ~50°C) temperature. Other preparations ensure that the atmosphere in the storage container will not alter (e.g., react with) the specimen.

For specimens with chemical or physical forms of crucial forensic value, the atmosphere in the storage container may be controlled. This typically involves packaging in an inert- or nitrogen-atmosphere glove box for specimens that are reactive in air. It also may involve packaging in an enclosure with controlled humidity.

Furthermore, the container itself must be selected to ensure that it will not react with the material and will protect it from ambient conditions in the storage facility. Specimens are canned in metal containers with metal-sealing surfaces (Donald and Kristo 2020). ORNL uses bespoke, stainless-steel (SS), bored-plug containers made by the Swagelok Company (Figure 2, *right*) and fitted with a blind SS gasket for packaging NNMA specimens. Containers are closed as recommended by the manufacturer but are not subjected to leak testing. Bored-plug containers are overpacked in an aluminum screw-top can (Figure 2, *left*) with SS wool inserted as padding.

Figure 2. Typical specimen package. A Swagelok bored-plug container (*right*) serves as the primary specimen confinement and is overpacked in an aluminum screw-top container (*left*) with SS wool padding.

Before they are bagged into the glove box, bored-plug containers are protected with plastic to reduce or prevent contamination on their external surfaces while in the glove box (Figure 3, *left*). Before and during filling, the can threads and lip are protected with a short plastic sleeve, which is taped at one end to the hexagonal portion of the can body, covers the threads, and blouses over the rim and part way into the container's neck (Figure 3, *upper right*). The can's lid is kept separate from the can until closing, which prevents tearing the plastic at the threads.

Figure 3. Plastic-protected bored-plug container. Protected container with funnel installed in preparation for filling with calcined ^{233}U oxide (*upper right*), with lid in place after removing plastic protecting threads (*left*), and during tightening using customized wrenches (*lower right*).

The short plastic sleeve protecting the threads is removed carefully between filling and screwing on the lid, but only after the nitrile gloves (the blue gloves shown in Figure 3, *lower right*) are replaced with a fresh pair over the glove box gauntlet gloves. The lid is secured using customized wrenches (Figure 3, *lower right*) before bagging out of the glove box. Immediately before bag out, the plastic and tape are peeled back most of the way from the can; then the can is slid out of the remaining plastic as it is dropped into a temporary overpack (e.g., a 1 L Nalgene, wide-mouth bottle) positioned in the bag port sleeve. After bag out, the can and overpack are moved to a radiological hood for decontamination. Typically, very little contamination is found on the can's exterior surfaces (assessable by smear), and any contamination that is present usually can be removed to transferrable alpha contamination levels of<20 dpm/100 cm^2.

Currently available bored-plug containers have limited sizes (¾ in. and 1 in. diameter bores, available at capacities up to ~100 cc), and they are used for small specimens (nominally up to ~100 g of heavy metal). This container meets anticipated canning needs at ORNL because specimens to be preserved are expected to contain less than 100 g and are in the form of powder or small solids that fit within the bores. If specimens exceed this capacity, more than one container may be used if the future. However, if specimens include large pieces exceeding the bore diameter, then a different primary can may be needed.

In addition to the above key steps for sampling specimens and preparing specimens for storage, other more mundane tasks must be performed to ensure the integrity of the sample and specimen. These tasks include

- cleaning the glove box used for sampling and canning to reduce chances of cross contamination with previously handled materials;
- calibrating and certifying a high-precision balance for nuclear material accountability;
- acquiring and cleaning tools for preparing the bulk material and acquiring the sample;
- acquiring, cleaning, and labeling sample vials and specimen cans;
- bagging tools, vials, cans, and the specimen (and the balance, if new) into the glove box; and
- bagging out samples, specimens, and waste.

Conclusions

Materials at ORNL that are of interest to the NNMA are being collected, sampled for characterization analyses, and packaged for long-term storage. Procedures used at ORNL will be considered for use at other DOE sites that are also sampling and preserving items for the NNMA.

References

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Watkins, R. W., S. J. Hensel, and J. M. Jordan, 2009. *Packaging and Transportation of Neptunium Oxide*, SRNS-STI-2009-00166, Aiken, SC: March 2009.