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PRODUCTION OF NDA WORKING REFERENCE MATERIALS FOR THE CAPABILITY EVALUATION PROJECT

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ABSTRACT

The production of Non Destructive Assay (NDA) Working Reference Materials (WRMs) that are traceable to nationally recognized standards was undertaken to support implementation of the Idaho National Engineering and Environmental Laboratory (INEEL) Nondestructive Waste Assay Capability Evaluation Project (CEP). The WRMs produced for the CEP project consist of Increased Am/Pu mass ratio (IAP) and depleted Uranium (DU) WRMs. The CEP IAP/DU WRM set provides radioactive material standards for use in combination with 55 gallon drum waste matrix surrogates for the assessment of waste NDA assay system performance. The Production of WRMs is a meticulous process that is not without certain trials and tribulations. Problems may arise at any of the various stages of WRM production which include, but are not limited to; material characterization (physical, chemical, and isotopic), material blend parameters, personnel radiation exposure, gas generation phenomenon, traceability to national standards, encapsulation, statistical evaluation of the data, and others. Presented here is an overall description of the process by which the CEP WRMs were produced and certified as well as discussions pertaining to some of the problems encountered and how they were solved.

INTRODUCTION

Non-destructive waste assay (NDA) methods are employed to determine the mass and α activity of waste-entrained radionuclides as part of the National TRU (Trans-Uranic) Waste Characterization Program. In support of this program the Idaho National Engineering and Environmental Laboratory (INEEL) Mixed Waste Focus Area (MWFA) developed a plan to acquire capability/performance data on systems proposed for NDA purposes. The Capability Evaluation Project (CEP) was designed to evaluate the NDA systems of commercial contractors by subjecting all participants to identical tests involving 55 gallon drum surrogates containing known quantities and distributions of radioactive materials in the form of sealed-source standards, referred to as working reference materials (WRMs).

Although numerous Pu WRMs already exist, the CEP WRM set allows for the evaluation of the capability and performance of systems with respect to waste types/configurations which contain increased amounts of ^{241}Am relative to weapons grade Pu, waste that is dominantly ^{241}Am, as well as wastes containing various proportions of depleted uranium. The CEP WRMs consist of a special mixture of PuO_2/AmO_2 (IAP) and diatomaceous earth (DE) or depleted uranium (DU) oxide and diatomaceous earth and were fabricated at Los Alamos National Laboratory (LANL). The IAP WRMs are contained inside a pair of welded inner and outer stainless steel containers. The DU WRMs are singly contained within a stainless steel container equivalent to the outer container of the IAP standards. This paper gives a general overview and discussion relating to the production and certification of the CEP WRMs.

WRM REQUIREMENTS

The statement of work (SOW)[1] provide by INEEL specified the objectives, task requirements, and technical specifications for the production of the CEP WRMs. WRM nuclear material masses are specified with the total allowable uncertainty at the 95% confidence level restricted to 0.75% for the IAP WRMS and 0.5% for the DU WRMs. α activity uncertainty is likewise restricted to 0.5%. Isotopic ranges and impurity level requirements within the nuclear materials are also specified in the SOW. At every step in the characterization and weighing of the nuclear materials that went into the WRMs, nationally recognized standards were used to ensure traceability to the National Institute of Standards and Technology (NIST) or NBL (New Brunswick Laboratory). Physical requirements of the nuclear materials included specifying the form of the materials (oxide powders) as well as placing constraints upon the particle size distribution of the powders. Additionally, specifications addressed the composition and form of the matrix material (DE), blend uniformity, containment (steel tubing), verification measurements, WRM shipping, and records disposition. Throughout every step in the characterization of the materials, production of the steel encapsulation assemblies, blending, filling, sealing (welding), WRM inspections, etc., quality assurance (QA) hold-points were invoked requiring appropriate documentation and "carefully specified QA and control measures to ensure data supporting attribute quantification, uncertainty and traceability are produced, analyzed and documented in an auditable form".[1]

Additional tasks required by the SOW[1] included the establishment of the required resources and personnel to complete the production of the CEP WRMs on schedule as well as develop contingency plans in the event of unanticipated delays. Formal procedures for every step of the CEP fabrication process were written, reviewed, and followed. Appropriate personnel were trained in QA procedures as well as technical procedures. Additional plans required by the SOW included a QA plan, a project management plan, and a documentation control and records plan. A final WRM Production Plan[2] was also written after certification of the WRMs and serves as a comprehensive and detailed description of all steps in the production of the WRMs.

RADIATION EXPOSURE

One of the main concerns when working with nuclear materials is the exposure of personnel to radiation. All possible precautions are taken to reduce the overall dose a worker may obtain during the production of the WRMs. Previous experience with Pu WRMs (dominantly ^{239}Pu) has indicated that the amounts of material used, combined with appropriate shielding and time minimization resulted in minimal exposure to personnel. However, the introduction of Am into the WRM production process greatly increases the potential hazard from radiation. The conbined γ and X-ray specific activities of ^{241}Am are approximately 55 times that of ^{239}Pu!

Coupled with the increased activity of the nuclear material was the requestor's original desire for a WRM containing nearly a gram of ^{241}Am. The NDA CEP production personnel had reservations and concerns regarding the quantities of Am specified in the SOW as the dose rate on a plastic blending bottle containing 900mg Am was measured at 10R/hr at contact! A steel WRM with this amount of Am would obviously have a lower dose rate but would still be high enough to pose several problems. Modeling calculations revealed that a WRM with approximately 54 mg of ^{241}Am would have a dose rate of about 500 mR/hr at contact and a 1 g Am WRM would have a dose rate near 9 R/hr. Actual measurement of a prototype 58 mg Am WRM revealed a dose rate of approximately 20 mR/hr at contact implying an actual dose rate for a 1 g Am WRM more on the order of 350 mR/hr. The Department of Energy's limit on exposure for radiological workers is 5 R/year (2 R/year for LANL) to the whole body and 50 R/year (30 R/year LANL) to the extremities. Obviously the high dose rates from a 1g Am WRM would severly limit its use on a regular basis and would also create problems relating to storage and shipping. In working with the INEEL it was decided to increase the number of WRMs (with smaller amounts of ^{241}Am) rather than produce one WRM with a large amount of ^{241}Am. By reducing the amount of ^{241}Am from the initially suggested 1g level to approximately 0.1g and by instituting a few relatively nonintrusive radiation exposure precautions, the maximum radiation dose any of the three persons fabricating the WRMs received was less than 100 mR total. Also, the highest measured dose rate from the WRMs containing the highest quantity of Am, 103 mg, was 28 mR/hr at contact and 10 mR/hr at 10 cm.

WRM PRODUCTION

Nuclear Material Preparation/Characterization

Plutonium oxide was initially prepared by the anion exchange purification of a plutonium nitrate solution, followed by precipitation as plutonium oxalate. The resultant Pu oxalate was calcined to PuO_2 and packaged in hermetically sealed food-pack cans.

Americium oxide was initially prepared by precipitating Am from solution using hydrogen peroxide. The Am hydroxide was dissolved in 7M HNO_3. Am was then separated from Pu via ion exchange. Am in the effluent was precipitated using oxalic acid. The Am oxalate was calcined to AmO_2 and screened through a 100 mesh screen and then packaged.

The depleted uranium oxide was initially prepared at Los Alamos as reactor fuel feedstock. U_3O_8 was dissolved in nitric acid. UO_4 was then precipitated using H_2O_2-NH_4OH. The precipitate was then filtered and dried to "yellow cake". The yellow cake was then calcined at 900°C for 16 hours in air to oxidize the material to U_3O_8. The U_3O_8 was then reduced to UO_2 by heating to 700°C for 1 hour in an H_2-Ar atmosphere. The temperature was then decreased to 400°C and the material oxidized in air for 6 hours. Further reduction of the U oxide was accomplished by heating the material to 700°C for 1 hour in H_2-Ar then sintering for 1 hour in CO_2 and allowed to cool in CO_2.

Preparation

The oxide materials were examined to determine if grinding would be required to produce a uniform grain size. All three oxide powders were of a suitable grain size and thus no grinding was necessary. Both the PuO_2 and the AmO_2 were calcined between 900°C and 960°C for several hours. The calcined PuO_2 was passed through a #80 mesh screen. All three oxides were individually blended for at least one hour to ensure a homogeneous powder from which samples were taken for chemical characterization, and particle size-distribution.

Characterization

Particle size distributions were performed on all three oxide powders in order to meet SOW specifications. These determinations were technical and QA hold-points. Each material was then assayed for total Pu, Am, or U as the case may be. Pu assay was determined by coulometric titration whereas the Am and U assays were accomplished employing isotope dilution mass spectrometry (IDMS). Isotopic distribution of each material was determined by thermal ionization mass spectrometry (TIMS). Impurities within each oxide were determined by one or more of the following: inductively coupled plasma mass spectrometry (ICP-MS), ICP-atomic emission spectroscopy (ICP-AES), ion chromatography, ion specific electrode, radiochemistry, and direct current arc spectroscopy. In addition, trace Pu and U within the Am oxide was determined by IDMS. Chemical analysis of the diluent (diatomaceous earth) was performed by glow discharge mass spectrometry. Each of these chemical analysis techniques are described in established LANL procedures and performed by trained personnel. All methods employ NIST- or NBL-traceable standards to maintain traceability to national standards. All determinations described above are technical and QA hold-points requiring input from INEEL before proceeding to the next stage of WRM production.

The chemical and isotopic analyses require the coordination of many analysts and strict oversight to ensure that results are traceable to national standards. Two areas of concern regarding the chemical and isotopic determinations include the mass balance of the AmO_2 and the traceability of the Am standard used in the isotopic and IDMS assay of the AmO_2. These challenges are described below.

A good internal check on the chemical analysis of a material is to add up all the constituents and determine if they total 100% by weight. Analysis of the AmO_2 (for those elements requested by INEEL) revealed that the total constituents summed to approximately 91.5%. This huge discrepancy would certainly discredit the use of this material as a working reference material unless it could be accounted for and explained. This rather large discrepancy came as a surprise as all of the major constituents were thought to have been included in the list of analytes requested in the SOW. Since Am oxide is rather hard to come by, it was determined to try to discover what unknown constituents accounted for the mass balance discrepancy instead of locating another source of Am oxide.

ICP-MS is a technique well suited to rapid qualitative scans for analytes within a mass range of 2-230 amu. Within 60 seconds or less, one can scan the entire mass range and identify the major constituents in a sample. A qualitative scan was performed on a sample of the AmO_2 to see if there were any high abundance elements that were overlooked. The elements Y and Np were present at high levels within the AmO_2. Subsequent quantitative analyses showed that these elements were present at 4.37% and 1.93 %, respectively. The Np is an α decay product of ^{241}Am. The source of the Y is unknown. While these two elements account for 6.3% of the missing mass, the total is still short of 100%. Additional scans verified the Y and Np but failed to reveal other constituents that would bring the total to 100%. Another alternative that was explored was that the AmO_2 had absorbed H_2O since it's production. This was evaluated by performing a Loss On Ignition (LOI). A sample of AmO_2 was placed into a Pt crucible and weighed. The crucible was then placed into an oven and heated to 950°C for 2 hours. After cooling the crucible was weighed again and the difference recorded. This exercise demonstrated that approximately 2% of the total weight of the AmO_2 was in fact absorbed H_2O. Thus the total constituents add up to 100.45 % (assuming stoichiometric oxygen of 11.72%) explaining the mass discrepancy.

The second area of concern regarding the chemical and isotopic analysis of the AmO_2 regards the traceability of the Am standard used in the Am assay and isotopic distribution determinations. IDMS offers a high-precision method for the determination of ^{241}Am in a wide variety of materials. IDMS uses a spike of another isotope of the element of interest as a sort of internal standard. In this case the spike used is a known quantity of ^{243}Am added to the samples. By measuring very precise isotope ratios (e.g., ^{241}Am/^{243}Am) one can then calculate the amount of ^{241}Am in the sample.

The ^{243}Am spikes are produced in large batches (200 or more) using a precision pipetting instrument which dispenses a certain amount of ^{243}Am (in solution) into individual glass vials. The spikes are then heated to dryness and stored until needed. Approximately 10% of the spikes produced are calibrated and the mean value obtained from those 10% is used as the amount of ^{243}Am in all 200 spikes. To calibrate the ^{243}Am spikes, a material in which the ^{241}Am content is accurately known must be available. For materials such as U and Pu, certified standards are available against which the spikes can be calibrated. However, for ^{241}Am, only very low concentration counting standards are available with NIST traceability. Ideally, one would prefer a pure and chemically assayed ^{241}Am material. Unfortunately, such a material is not available and would be very expensive to produce. This creates a problem for the CEP WRMs as all chemical and isotopic results must be traceable to nationally recognized standards. To address this problem a Pu material (Sample 17709), in which the ^{241}Pu has been accurately measured (using NBL-certified Pu isotopic standards), is used as a source of small, but known quantities of ^{241}Am (based on the decay of ^{241}Pu to ^{241}Am). Using this known amount of ^{241}Am, the amount of ^{243}Am in the spikes was determined to be 1.19235 μg ^{243}Am/spike (12 of the spikes were calibrated using 12 separate samples of 17709, i.e., n=12).

This value was then verified using three different materials as independent checks on the calibration of the ^{243}Am spikes. In one case, another Pu material (Sample 55600) was used in the same manner as that for sample 17709 described above. Secondly, an available NIST Standard Reference Material (SRM) Am solution radiochemistry counting standard (SRM 4322—with certified values) was used to calibrate the ^{243}Am spikes. Thirdly, a European certified Am solution radiochemistry standard (Amersham, AMP 10040) was likewise used to calibrate the ^{243}Am spikes. Good agreement was obtained between these three calibrations and the initial calibration (Table 1, Fig. 1). Traceability is documented through the use of NBL-certified Pu isotopic standards (Samples 17709 and 55600) and NIST-certified SRM 4322.

Table 1. Results of ^{243}Am Spike Calibration

Based on decay of ^{241}Pu to ^{241}Am in Sample 55600

Spike #	µg ^{243}Am
70	1.1934
103	1.1918
146	1.1929
178	1.1930

Mean	Std. Dev.	% RSD
1.1928	0.0007	0.0574

NIST SRM 4322

Spike #	µg ^{243}Am
87	1.1958
150	1.1926
201	1.1915

Mean	Std. Dev.	% RSD
1.1933	0.0022	0.1872

Amersham (AMP10040)

Spike #	µg ^{243}Am
5	1.1953
55	1.1947
145	1.1946
185	1.1943

Mean	Std. Dev.	% RSD
1.1947	0.0004	0.0351

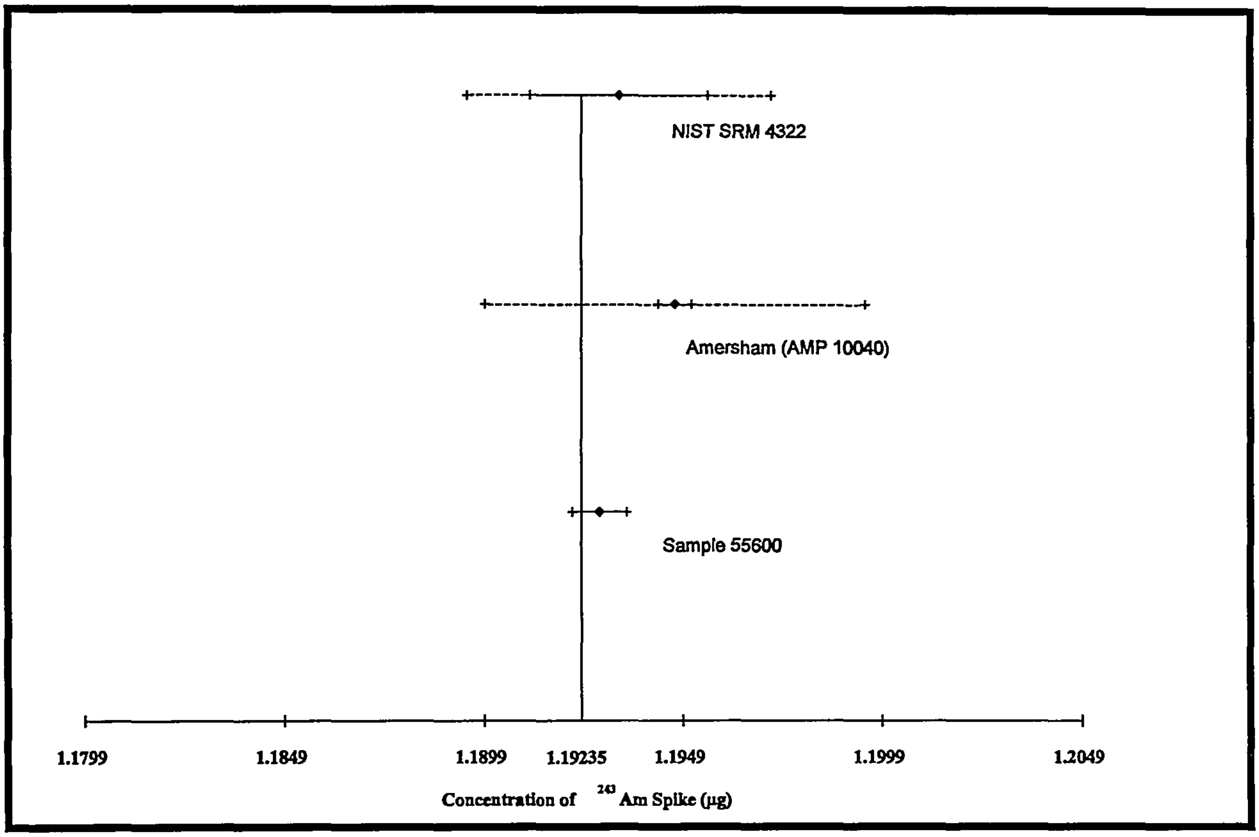

Fig. 1. Comparison of results for ^{243}Am spike calibration. Dashed lines represent ±1σ of the certified values, solid lines represent ±1 σ of the measured values.

Blend Parameters and Evaluations

To establish the blender speed and length of time required to produce homogeneous blends of nuclear material with DE, cold tests were initially performed using iron powder as a surrogate for the nuclear material.[3] Following this, actual test blends using PuO_2 and DE were prepared following established LANL procedures. Blend parameters specified in the SOW require that the blend be uniform to within ±2.5 % of the mean concentration for any given 30 cm^3 volume and is a QA hold-point. The homogeneity of these blends was determined via γ-ray spectrometry to be better than 2 % RSD. Concerns of nuclear material particle agglomeration during blending were evaluated by performing a particle size distribution analysis of the PuO_2 and of the PuO_2-DE blend. No indication of agglomeration of the nuclear material particles was found.

The α-neutron yield of the blend was also evaluated employing a Shuffler neutron assay instrument (passive mode). A prototype IAP WRM (58 mg Am) was analyzed with results indicating that the coincidence neutron counts per second of the WRM were indistinguishable from background. However, the singles neutron count rate of the 58 mg Am WRM was about 150 counts per second, roughly five times background.[2] These data were reviewed by the NDA CEP Technical Team and was a technical hold-point prior to the preparation of IAP WRMs.

Gas generation within the IAP WRMs due to α radiolysis of hydrogenous material was evaluated through computational studies.[3] These studies reveal that the pressure within the WRMs will rise to 22.6 psig within 27.9 years due primarily to the radiolysis of residual water. After 27.9 years the water will be consumed and the pressure will continue to rise very slowly due to formation of helium gas formed by the decay of α-emitting radionuclides. The pressure within the stainless steel WRMs will reach the maximum design and failure (yield) pressures within 83 and 176 years, respectively. These data were reviewed by the NDA CEP Technical Team and was a technical hold-point prior to the preparation of IAP WRMs.

Since depleted uranium has a α activity at least three orders of magnitude less than the IAP WRMs, α-n reactions and gas generation was not evaluated for the DU WRMs.

Blending

A Turbula Model T2C blender, shown in Fig. 2., was used for blending. Separate blends were prepared for each individual WRM to ensure that the amount of nuclear material in each WRM was known with maximum certainty. Prior to producing the first IAP blend, the quantity of DE required to fill a tap-packed stainless steel container to within 0.5 ± 0.05 inches of the top was determined (in cold testing and based on experience with the production of Pu WRMs) to be 134.0 g. The DE was weighed out to the nearest 0.1 g and recorded. The DE was then placed in a uniquely identified blend container. The containers were introduced into the glovebox train and transferred into the weighing glovebox. Weighed quantities of PuO_2 and AmO_2 were transferred to the blend bottle containing the DE. After DE, AmO_2, and PuO_2 addition, the blend container lid was secured,

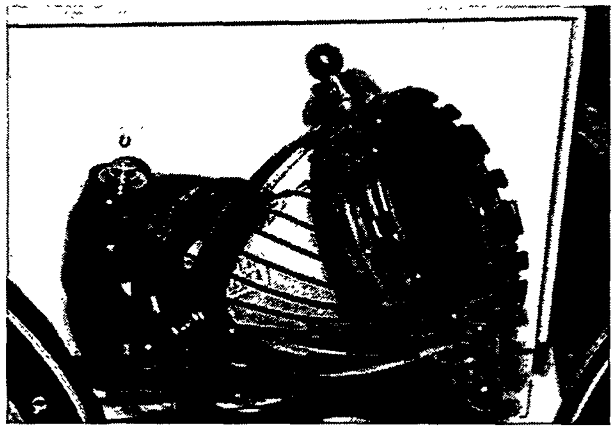

Fig. 2. Turbula blender with blend bottle.

and the container was removed from the weighing glovebox, transferred into the blending glovebox, and introduced into the blender. Blending was performed for 60 minutes at the medium rotational speed of the Turbula Blender. The homogeneity of the blends was verified via γ spectrometry of multiple samples of the blend.

The DU blends were prepared in essentially the same manner as the IAP blends. However, since the DU WRMs have such large mass ranges for U, the amount of DE in these WRMs is far less than the amount of nuclear material (opposite from the IAP WRMs). Thus, errors were encountered in terms of the proper amount of DE to use. The amount of DE was estimated based on the following equation which was successfully used for the IAP WRMs:

mass of DE = density of DE * (volume of WRM - mass of nuclear material/density of nuclear material)

Unfortunately it was discovered that the relationship between the amount of DE to the amount of UO_2 required to fill the WRM cylinder was not linear. Thus, in most instances, there was left-over UO_2/DE blend. This remaining blend was weighed and subtracted from the total so as to determine the amount of UO_2 in the WRM. This additional step and the errors associated with it were later captured in the error propagation and the determination of the total error placed on the amount of UO_2 in the WRM and its α activity. The homogeneity of the DU/DE blends was verified via γ spectrometry.

Steel Assemblies

Sixteen stainless steel assemblies were fabricated from #304 stainless steel tubing (seamless) and sheet and bar stock in the same manner as those prepared for other WRMs previously manufactured.[3] The fabrication was performed at the LANL main machine shop as described in the SOW.[3] The assemblies consist of partially completed steel tubes that have been helium leak checked. All QA documentation regarding the fabrication and leak checking are maintained in the NDA CEP WRM files.

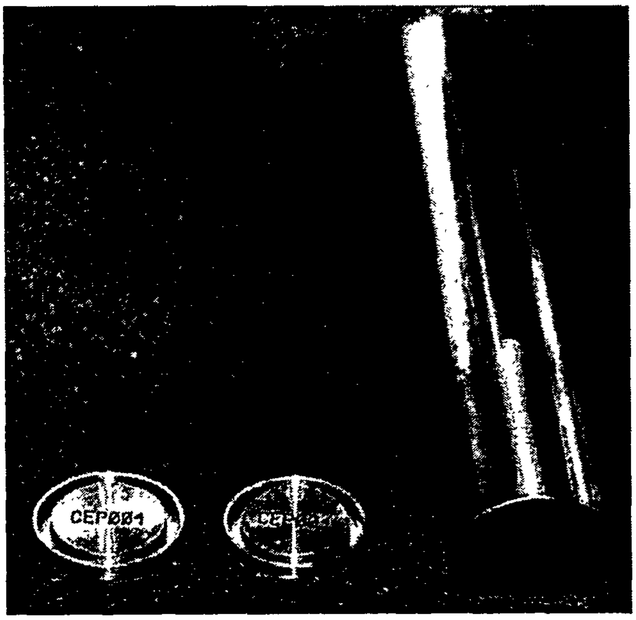

Fig. 3. DU WRM Steel assembly. Length of steel tube ≈ 9 inches.

The sixteen, #304 stainless steel tubing assemblies and upper endcaps were inspected for cleanliness, identification marks, dimensions (wall thickness, length, diameter), endcap fit, damage, and weld quality. Inspection was performed following established procedures. Initialed and dated inspection forms for all assembly inspections are retained in the NDA CEP WRM files. The 16 assemblies were identified with the following sequential alpha-numeric system: CEP-001, ..., CEP-010, ...CEP-016. The identification was laser-etched into both the assembly inner and outer cylinder endcaps for the IAP WRMs and the outer assembly and endcap for the DU WRMs (Note: the DU WRMs are singly contained). Figure 3 shows a labeled DU WRM assembly with endcaps.

Filling

To minimize the spread of contamination, the cylinders were wrapped in aluminum foil and taped in a manner to cover all the cylinder outer surfaces while leaving the open end of the tube exposed for filling. The tube was then placed in the filling glovebox. The cylinder was fitted with a plastic sleeve which covered the lip of the open end and extended 12 mm down into the cylinder. This sleeve prevented blend powder from contacting the upper 12 mm of the cylinder, where the graphite frit and endcap would be placed.

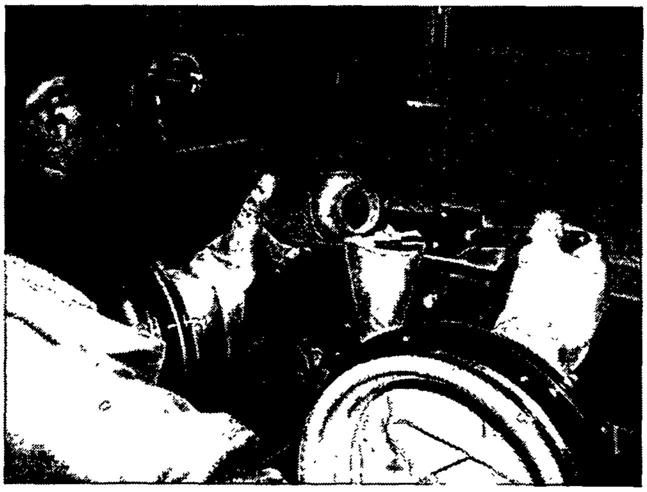

Fig. 4. Filling steel cylinder with blend.

For stability, the cylinders were placed inside an approximately 6 cm (ID) graduated cylinder of about 15 cm in height. An approximately 30 x 30 cm sheet of brown paper was positioned under the graduated cylinder so that any spillage could be readily detected and recovered. Tests with DE demonstrated that 1 mg of DE (<0.001% of the blend mass) was highly visible when spilled on this paper. All implements used in the loading process were kept on the paper. A paper funnel was then inserted into the open cylinder and the designated blend powder was added incrementally via a spatula into the cylinder. After each incremental addition, the cylinder was repetitively tapped against the glovebox floor to firmly pack the powder. Figure 4 shows the incremental addition of blend powder into a cylinder.

To prevent loss of blend powder during tap-packing, a small watch glass was held over the open end of the cylinder. Any detected spillage was immediately returned to the blend bottle or the cylinder. The incremental addition and tap packing steps were continued until all the blend powder was introduced into the cylinder (Note: For some of the DU WRMs, not all of the blend was transferred into the cylinder due to errors in determining the proper amount of DE to use for blending. Since not all of the blend is incorporated into the WRM, the total mass of DU in the WRM was adjusted and the homogeneity of the blend was determined and incorporated into the total uncertainty calculations.). The cylinder was finally tap packed until the surface of the powder was just below the bottom lip of the plastic sleeve insert. Figure 5 shows a fully loaded and tap-packed cylinder ready for graphite frit insertion.

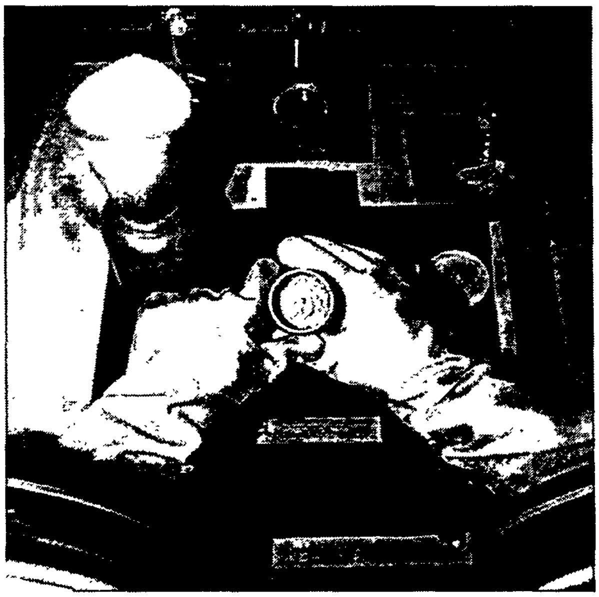

Fig. 5. Tap-packing the blend into the steel cylinder.

After the blend powder was transferred into the cylinder, the plastic sleeve was removed and a pre-cut graphite felt frit was carefully inserted and gently pressed down onto the surface of the powder. The loaded WRM cylinder was now ready for bagout from the glovebox. For the IAP WRMs, after each cylinder was fully loaded, the paper funnel, paper tissues used to clean the plastic sleeve, watch glass, and spatula, and the paper sheet under the loading area were inserted into the now-empty blending bottle. For the DU WRMs, these materials were inserted a CLEAN blending bottle (except for CEP011 which was handled like the IAP WRMs discussed above). The blending bottles and contents were then bagged out of the filling glovebox and submitted to radiochemistry to determine the amount of nuclear material adhering to these materials (NM hold-up). This measurement was performed using the far-field γ counting method following established LANL procedures. The amount of NM hold-up is accounted for and integrated into the final nuclear material masses and associated uncertainties. QA documentation regarding the NM hold-up is required by the SOW and is kept in the NDA CEP WRM files.

Inerting

The prepared IAP WRM cylinders were transferred into the inert gas airlock of the welding glovebox. The airlock was gently evacuated and backfilled with helium gas. The evacuation and backfilling operation was repeated twice. This operation replaced the air in the cylinders with helium, which prevented oxidation of the stainless steel cylinders during welding and acted as a fill gas for leak inspection after welding.

To preclude Pu contamination of the DU WRMs from the above mentioned airlock, the prepared DU WRM cylinders were transferred into a large desiccator which was then evacuated using a rotary pump. The desiccator was then backfilled with helium gas. The evacuation and back filling was repeated twice. This operation replaced the air in the cylinders with helium which acted as a fill gas for leak inspection. Figure 6 shows the desiccator with the DU WRMs.

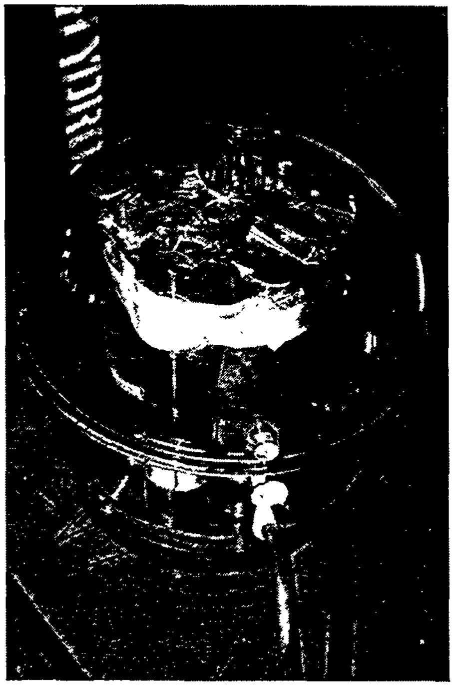

Fig. 6. DU WRMs backfilled with helium gas.

Welding

A Programmable TIG (Tungsten/Inert Gas) welder located within an inert atmosphere glovebox was used to perform the TIG welds on the inner stainless steel tubes for the IAP WRMs. A similar TIG welder mounted on a bench top was used to seal both the outer IAP and the DU cylinders. Figure 7 shows the in-glovebox welding apparatus with an IAP inner cylinder ready for welding.

Using the #304 stainless steel cylinders and end caps that comprised the test components, practice welds were performed to establish welding power supply amperage,

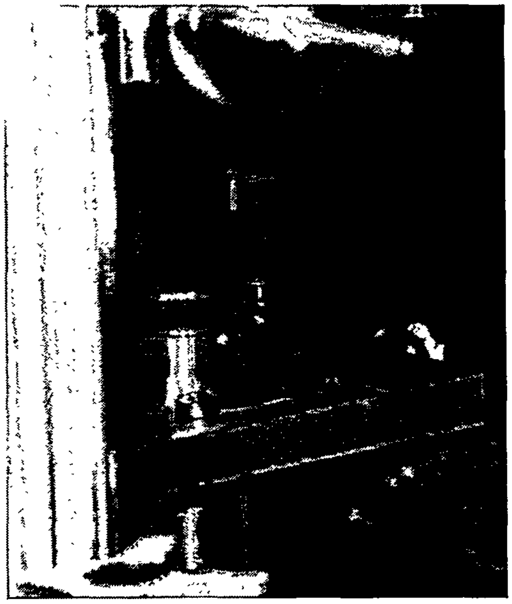

Fig. 7. IAP WRM undergoing welding operation.

program cylinder rotational speed, and welding electrode-to-cylinder distance and position following established LANL procedures. To ensure acceptable welds, end cap welds were performed at different current levels, and a current operating range was established. These parameters were established for both the inner and outer cylinders and end caps.

Fig. 8. Endcap weld cross section.

The welding equipment, welding parameters, welding procedure and weld operators were qualified as detailed in LANL procedures. Once they had demonstrated operational welding parameters by performing test welds, the welding operators performed qualification welds on both the inner and outer cylinders with appropriate end caps. The welds extended 360° around the cylinders, with adequate over-run to assure a complete seal and controlled arc break. The weld qualification acceptance criteria includes visual examination at 10x magnification, helium leak testing, and metallographic examination as defined in established LANL procedures. Figure 8 shows a photomicrograph of an inner-cylinder endcap weld cross-section with 0.040" penetration. Weld configuration and associated parameters were QA hold-points.

Decontamination

After the inner cylinder end caps (IAP WRMs) were welded in the inert atmosphere glovebox, the cylinders were removed from the glovebox through a series of cleaning operations. The cleaning was assessed by smearing the cylinders with a Health Physics swipe cloth, and then counting the swipe in an α swipe counter. Once the cylinders were cleaned to <20 disintegrations per minute (dpm) smearable α contamination, they were removed from the open-front glovebox and placed in plastic bags. The cleaning and contamination monitoring was performed following established LANL procedures. Records of the decontamination assessment are retained in the NDA CEP WRM files.

Leak Check

Helium leak checks were performed on the inner cylinder welds for every IAP WRM and the cylinder welds for the DU WRMs. The helium leak checks were performed following established LANL procedures with a leak rate pass criteria of $< 1 \times 10^{-8}$ atm-cc/second. All cylinders demonstrated a helium leak rate of $< 1 \times 10^{-8}$ atm-cc/second, meeting Department of Transportation requirements for shipping in Class B containment. QA documentation was required for the helium leak checks.

Final Inspection

Final WRM inspections included α contamination checks, dimensional checks, and γ-ray measurements to both evaluate WRM nuclear material uniformity, and verify WRM nuclear material loadings. Each WRM was placed in a plastic bag and sealed after final inspection. The bags were identified using a flow-pen with the same alpha-numeric identifier as the WRM.

Thorough α contamination measurements were made on every WRM using both swipe methods sensitive to 6 dpm/100 cm^2 removable α activity, and direct α surveys sensitive to 300 dpm/100 cm^2. No detectable α contamination was found on any WRM. These survey results were recorded, signed, and dated for every WRM and are contained in the NDA CEP WRM files.

Every WRM was checked for length and diameter to ensure a length of 8.99-9.01 inches and a diameter of 1.940-1.947 inches. The final weld on the endcap of the outer cylinder added up to 0.04 inches to the length of some of the WRMs. With permission from the INEEL technical manager, this increased length was accepted as being preferable to machining the weld down to the 9.01 inch specification length. Further, every WRM was visually inspected for any obvious defects such as dents or scratches, and to ensure the identification markings were clear and robust. These data are recorded, dated, signed, and retained in the NDA CEP WRM files.

Each WRM was subjected to collimated γ-ray intensity measurements focused on either a 4.5 cm zone of the left and right (upper and lower if the cylinder is vertically oriented) segments of the cylinder (IAP WRMs) or three 5 cm segments near the center of the WRM (DU WRMs). These measurements were used to determine the uniformity of the nuclear material within the WRM and to verify the contents of the WRM. For the IAP WRMs, the value obtained for the left side of the WRM is divided by the value for the right. A uniform distribution of nuclear material would yield a ratio of L/R = 1. In no case was the L/R ratio significantly different from the mean (1.01 ± 0.02).

The same measurements used above for uniformity were also applied to the verification of the nuclear material content of the IAP WRMs. The left and right side counts are added together which is then divided by the total mass of the Am or Pu contributing the γ peak. By dividing the total peak areas by the mass of nuclear material, one would expect a constant count rate/mass value for all the WRMs. In no case was the Count Rate/Mass significantly different from the mean.

The DU WRMs were counted on a segmented γ scanner. Instead of counting the left and right halves of each WRM as was done for the IAP WRMs, three 5 cm segments were counted (2 hours/segment) and compared for each DU WRM. Acquiring accurate data for the DU WRMs was problematic due to the weak γ signal from the ^{235}U coupled with an excessive attenuation correction applied to the count data. The attenuation correction in most cases was > 90% thus rendering the quality of the data suspect. Even with the poor quality count data it is evident that the WRMs are uniform to better than 18% (worst case). Higher quality γ count data would likely show uniformity to better than 10%.

The same measurements used above for uniformity were also applied to the verification of the uranium content of the WRMs. The three segment counts are added together and then divided by the total mass of U. In one case the Count Rate/Mass was apparently different from the mean. This was to be expected as this WRM has a DE/DU mass ratio approximately ½ that of the other DU WRMs, hence a lower attenuation of the 186 keV γ due to self-shielding. The other five DU WRMs, taken as a group, show no significant deviation from the mean which verifies the U content of the WRMs.

WRM CERTIFICATION

Nuclear Material Mass and α Activity

The WRM production process was designed to meet all SOW specified design attributes. To certify the WRMs, critical information and data generated during the WRM production process was formally documented, filed, and reduced through appropriate calculations to determine the Pu, Am, and U mass values and the total α activity for each WRM. Further, uncertainty data for critical information was propagated to determine the statistical uncertainties of the calculated masses and α activities of each completed WRM.

Finally, for certification purposes, all critical measurements are traceable to nationally recognized reference materials.

Nuclear Material Mass

The calculation algorithms for Pu, Am, and U mass and α activity for the WRMs are presented below. These calculations were executed in spreadsheet format. It should be noted that the AmO_2 used for CEP WRM production does contain minor amounts of Pu, U, and Np. The small concentration of these elements in the AmO_2 result in negligible contributions to the total α activity and are hence ignored in the mass and α activity calculations.

The Pu mass for each WRM is calculated as follows:

Pu Mass (g) = (Wt. PuO_2 (g) x Pu assay) - T&H Loss (g Pu)

where: Wt. PuO_2 is the weight of PuO_2 (g) weighed out for the specific WRM.
Pu assay is the mean value of the Pu content of the PuO_2 in g Pu/g PuO_2 (decay corrected to 6/1/97).
T&H Loss is the transfer and hold-up loss as determined by the γ spectrometry assay of the blending container, funnel, cleaning tissues, and the transfer spillage catch paper.

The ^{241}Am mass for each WRM is calculated as follows:

^{241}Am Mass (g) = [(Wt. AmO_2 (g) x Am assay1) + (Wt. Pu (g) x Am assay2)] - T&H Loss (g Am)

where: Wt. AmO_2 is the weight of AmO_2 weighed out for the specific WRM.
Am assay1 is the mean value of the Am content of the AmO_2 in g Am/g AmO_2 (decay corrected to 6/1/97).
Wt. Pu is the weight of elemental Pu in the WRM (i.e., Wt. PuO_2 (g) x Pu assay).
Am assay2 is the mean value of the Am content of the PuO_2 in g Am/g Pu (decay corrected to 6/1/97).
T&H Loss is the transfer and hold-up loss as determined by the γ spectrometry assay of the blending container, funnel, cleaning tissues, and the transfer spillage catch paper.

The DU mass for each WRM is calculated as follows:

DU Mass = (Wt. UO_2 x U assay) - T&H Loss (g U)

where: Wt. UO_2 is the weight of UO_2 weighed out for the specific WRM.
U Assay is the mean value of the U content of the UO_2 in g U/g UO_2.
T&H Loss is the transfer and hold-up loss as determined by the γ spectrometry assay of the blending container, funnel, cleaning tissues, and the transfer spillage catch paper.

α Activity

The WRM α activity is the summation of the α activity contribution from each of the Pu, Am, and U isotopes in the WRM. To determine the α activity for each WRM, the α specific activity (α curies per gram Pu, Am, or U multiplied by the g Pu, Am, or U, respectively) for the nuclear material feed stock was calculated, effective 6/1/97 (See Table 2). Each WRM total α activity was calculated by multiplying the WRM Pu, Am, or U isotopic mass times the appropriate factor (see Table 2) and summing all the activities together.

Table 2. Atomic Masses, Half-Lives, and α Activities of the Isotopes Present in the CEP WRMs.

Isotope	At. Mass (a.m.u.)	At. Mass Uncert. (a.m.u.)	$T_{1/2}$ (yrs)	$T_{1/2}$ Uncert. (yrs)	$T_{1/2}$ (s)	Total Specific Activity (Ci/g)	Branching Ratio % α	α Activity (Ci/g)
^{233}U	233.03963	3.006E-06	1.592E+05	2.0E+02	5.021E+12	9.644E-03	100	9.644E-03
^{234}U	234.04095	2.147E-06	2.455E+05	6.0E+02	7.742E+12	6.227E-03	100	6.227E-03
^{235}U	235.04392	2.147E-06	7.038E+08	5.0E+05	2.220E+16	2.163E-06	100	2.163E-06
^{236}U	236.04556	2.040E-06	2.342E+07	3.0E+04	7.386E+14	6.472E-05	100	6.472E-05
^{238}U	238.05078	2.147E-06	4.468E+09	3.0E+06	1.409E+17	3.364E-07	100	3.364E-07
^{238}Pu	238.04955	2.147E-06	8.770E+01	3.0E-01	2.766E+09	1.714E+01	100	1.714E+01
^{239}Pu	239.05216	2.147E-06	2.411E+04	3.0E+01	7.603E+11	6.208E-02	100	6.208E-02
^{240}Pu	240.05381	2.040E-06	6.563E+03	7.0E+00	2.070E+11	2.271E-01	100	2.271E-01
^{241}Pu	241.05685	2.040E-06	1.435E+01	1.0E-01	4.525E+08	1.034E+02	0.0025	2.534E-03
^{242}Pu	242.05874	2.147E-06	3.733E+05	1.2E+03	1.177E+13	3.960E-03	100	3.960E-03
^{241}Am	241.05682	2.147E-06	4.322E+02	7.0E-01	1.363E+10	3.434E+00	100	3.434E+00
Ref:	4	4	5	5	5		5	

Uncertainty

To meet the SOW section 4.1 criteria for α activity and uncertainty, the following information was collected and data reduction performed.

Weighing Uncertainty

Random uncertainties for weighing were estimated from repeated weighings using a certified standard weight that most closely matched the weight of the target quantity of nuclear material. These weighings were performed on certified balbnces before each set of same-target-mass nuclear material was weighed. The balance performance is summarized in Table 3 below.

Table 3. Precision on Standard-Control Weight Weighings.

Diatomaceous Earth Weighings
Balance: 13045 (Certified)
Check Wts: Cenco Class S (Certified)

Standard Wt.	Number of Measurements	Mean	Std. Dev.	% Uncert.
30 g	15	29.99853	5.16E-04	0.009
50 g	3	50.001	0.002	0.014
100 g	20	99.993	0.004	0.018

Diatomaceous Earth Adjustment Weighings (DU WRMs)
Balance: 015233(Certified)
Check Wts: Not Certified

Standard Wt.	Number of Measurements	Mean	Std. Dev.	% Uncert.
10 g	15	10.00094	1.46E-05	0.010
200 g	12	200.0143	4.93E-05	0.007

Pu Oxide and Am Oxide Weighings
Balance: 013599 (Certified)
Check Wts: 15082 (Certified)

Standard Wt.	Number of Measurements	Mean	Std. Dev.	% Uncert.
10 mg	5	0.01001	4.47E-06	0.204
50 mg	5	0.05002	5.48E-06	0.062
100 mg	10	0.10002	6.75E-06	0.032
1 g	6	1.00001	5.16E-06	0.003
2 g	10	2.00003	6.75E-06	0.002

U Oxide Weighings
Balance: 016834 (Certified)
Check Wts: 4482,3648 (Certified)

Standard Wt.	Number of Measurements	Mean	Std. Dev.	% Uncert.
500 g	41	499.954	5.91E-03	0.012
1 kg	38	999.899	6.49E-03	0.012

The standard weight sets used for control weighings of the nuclear materials were certified against NIST traceable weights. The observed control weight checks (Table 3) show no statistically significant bias from the certified mass. Hence, the WRM nuclear material weights were considered free of significant bias.

Assay Uncertainty

The mean assay value of the five PuO_2 samples is 0.87804 (on 6/1/97). The precision of these replicates has a relative standard deviation of 0.033%. Since there were five analyses, the 95% confidence bound on the PuO_2 assay is 0.036%.

The ^{241}Am assay (of the PuO_2) has a one random standard deviation uncertainty of 0.028 %. As described above, the IDMS method uses a ^{243}Am spike as an internal standard. The uncertainties reported for the European and NIST standards (± 0.8%) used to calibrate the ^{243}Am spike are much larger than the inherent uncertianty of the mass spectrometry results. Therefore the relative uncertainty of the mass spectrometry results are conservatively estimated at 0.25% at the 95% confidence level. This estimate is based on the original calibration of the ^{243}Am spike (EDTA titration of a high purity ^{241}Am material) along with the data presented earlier. The 0.25% serves as a systematic error as applied to the Am assay. The random error of 0.028% (obtained from multiple determinations of the Am assay) is added after using the systematic error to bound the expected value resulting in an overall error of 2.8 µg Am/g Pu.

Four samples of Am oxide were also assayed by IDMS. The mean ^{241}Am assay value (amount of ^{241}Am in the AmO_2) of 0.78728 (on 6/1/97) has a one random standard deviation uncertainty of 0.284%. Again, since no nationally traceable mass spectrometry (isotopic) standards exist for Am, the relative uncertainty of the ^{243}Am spike solution concentration has been conservatively estimated as 0.25% at 95% confidence as described above. The random uncertainty associated with this assay is 0.28% as obtained from multiple determinations (four by IDMS) of the Am content of the AmO_2. The random error (0.28%) is added after using the systematic error (0.25%) to bound the expected value resulting in an overall error of 0.6%.

The uncertainty on the U assay (0.87493) of the UO_2 at the 95% confidence level is taken as the standard deviation of the five assay values divided by the square root of five. This is then multiplied by the corresponding student's t value for n = 5 to obtain the 95% confidence bounds. The overall error on the U assay is calculated as 0.03%. Thus the overall error is consitent with that observed for the long-term analyses of uranium standard NBS SRM U005.

Isotopic Uncertainty

The Total Evaporation Mass Spectrometric method used for the Pu and U isotopic distribution analyses is an absolute method with no known bias. The method was calibrated with the Plutonium Isotopic Standard NBS SRM 948 (NBS is now NBL), which has a Pu distribution similar to the PuO_2 starting material. The five samples of PuO_2 analyzed for total plutonium (by coulometry) were also analyzed for Pu isotopic distribution using TIMS. The summary statistics provide estimates of isotopic standard deviations that were 25 to 67% less than the standard deviations obtained on the measurement control standard (NBS 948), measured over a four month period immediately prior to the date of the PuO_2 isotopic measurements. To be conservative, it was decided to use the isotopic averages of the five samples of PuO_2 and the standard deviations calculated from the four month measurement control data. To obtain the standard deviations of the averages, the measurement control standard deviations were divided by the square root of five, the sample size. These estimates of uncertainties for the stated PuO_2 isotope weight percents are then multiplied by the corresponding student's t value for n = 5 to provide 95% confidence bounds (CB), and are listed in Table 4.

Table 4. Upper Bound Error Estimates for Mass Spectrometric Pu Isotopic Distribution.

Isotope	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu
Mean	0.0143	93.7811	5.9448	0.2038	0.0560
Std. Dev	0.0014	0.0022	0.0008	0.0015	0.0003
95% C.B.	±0.0018	±0.0028	±0.0010	±0.0019	±0.0003

The same method used for the Pu isotopic distribution was also employed for the U isotopic distribution of the UO_2. The method was calibrated with the Uranium Isotopic Standard NBS SRM U005, which has a U distribution similar to the UO_2 starting material. The five samples analyzed for total uranium were also analyzed for U isotopic fraction using TIMS. The summary statistics provide estimates of isotopic standard deviations that were generally similar to the standard deviations obtained on the measurement control standard (NBS SRM U005), measured over a 1.5 year period immediately prior to the date of the UO_2 isotopic measurements. It was decided to use the isotopic averages of the five samples of UO_2 along with their standard deviations. These estimates of uncertainties for the stated UO_2 isotope weight are divided by the square root of five and then multiplied by the corresponding student's t value for n = 5 to provide the 95% confidence bound and are listed in Table 5.

Table 5. Upper Bound Error Estimates for Mass Spectrometric U Isotopic Distribution.

Isotope	^{233}U	^{234}U	^{235}U	^{236}U	^{238}U
Mean	0.0000	0.0008	0.1902	0.0034	99.8057
Std. Dev	0.0000	0.0004	0.0004	0.0003	0.0005
95% C.B.	±0.0000	±0.0005	±0.0004	±0.0004	±0.007

Transfer and Hold-Up Loss

Transfer and hold-up loss quantities were measured by counting the 59.5 keV γ peak of the ^{241}Am (IAP WRMs) and the 63.32 keV γ peak of ^{234}Th (DU WRMs) contained in the funnels, cleaning tissues, and spillage catch paper used to transfer the blend material into the stainless steel cylinder. For the IAP WRMs, since all of the blend produced was incorporated into the steel cylinders, the blending bottle was also counted to determine the amount of Am and Pu that was adhered to the blending bottle. For the DU WRMs, the blending bottle was not counted (except for CEP011). This is because there was always a portion of the blend that was not incorporated into the WRMs (except for CEP011 in which all of the blend was incorporated into the WRM) and this excess amount of blend was determined by weight and the amount of U in the WRM was adjusted accordingly. These loss corrections were relatively small; the largest loss was 0.063 % for WRM CEP003.

α Activity Uncertainty

α half-life values for converting Pu, Am, and U isotope quantities in the WRMs to α activity are those presented in Table 2. The total α activity for the various WRMs has two uncertainty components, the α half-life and the isotopic abundance. These uncertainty terms are incorporated into the total uncertainty associated with the total α activity of each WRM.

Combined Uncertainty for Mass and α Activity

Standard uncertainty estimation methods were used to calculate individual random and systematic uncertainties for Pu, PuO_2, Am, AmO_2, U, and UO_2 mass, total α activity, and Pu and U isotope ratios. Propagation of variance (POV) techniques were used to appropriately combine the uncertainties for all the components used to calculate nuclear quantities. Where well-supported estimates on uncertainties for components were not available, a conservative approach was taken to use values that are believed to exceed the actual values. Therefore the 95% confidence intervals (bounds) listed on the WRM Certificates are believed to be larger than they would be if exhaustive data was available for every uncertainty component. Identified in Table 6 are uncertainty components included in estimates of the 95% confidence interval for the nuclear quantities listed on the WRM Certificates.

Table 6. Components included in the total uncertainty estimates for the CEP WRMs.

	Weighing	**Pu, Am, or U Assay**	**Pu or U Isotopic Ratio**	**Transfer & Hold-up**	**Homogeneity**
PuO_2 Mass	X				
Pu Mass	X	X		X	
Pu Isotopic			X		
AmO_2 Mass	X				
Am Mass	X	X		X	
UO_2 Mass	X				X
U Mass	X	X		X	X
U Isotopic			X		X
α Activity	X	X	X	X	X

Certification

Content and Traceability Certificates for each WRM were prepared, signed and dated by the LANL Analytical Chemistry (NMT-1) Group Leader and the LANL Project Leader for NDA CEP WRM production. The reduction of PuO_2, AmO_2, and UO_2 characterization, mass transfer data, and control data generated during the production of the WRMs produces Pu, Am, and U isotope mass and α activity, as well as uncertainty data required for WRM certification. These data and calculations are formally recorded, signed and stored in the NDA CEP WRM files. Certification also requires that the critical characterization measurements (Pu assay, Pu isotopic distribution, Am assay, PuO_2, AmO_2, and UO_2 weighings, U assay, and U isotopic distribution) be traceable to nationally recognized reference materials. This traceability has been demonstrated by identifying these reference materials on the formal certificates and in the analytical procedures used. INEEL received the Certificates of Content and Traceability for these WRMs. Copies of these reference materials' certificates are retained in the NDA CEP WRM files. To the highest degree possible, traceability to nationally recognized reference materials was established for less critical parameters, including particle size analysis, impurity analyses, isotope half-life and α specific activity, and helium leak check. Certificates or statements addressing traceability are retained in the NDA CEP WRM files for the less critical parameters.

CONCLUSIONS

The production of working reference materials is a highly involved and controlled process. Extreme care is taken at all stages to ensure quality assurance requirements are met and that the finished reference materials are traceable to national standards. In conjunction with existing Pu WRMs, the CEP WRM set will allow for the evaluation of the capability and performance of systems with respect to waste types/configurations which contain increased amounts of ^{241}Am relative to weapons grade Pu, waste that is dominantly ^{241}Am, as well as wastes containing various proportions of depleted uranium. These WRMS are valuable resources that will undoubtably be employed in other future endeavors following the conclusion of the CEP project.

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