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Lawrence Livermore National Laboratory Measurements of Plutonium-bearing Oxide in DOE-STD-3013-2000 Containers Using Calorimetry and Gamma Isotopic Analyses

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Abstract

Lawrence Livermore National Laboratory (LLNL) routinely uses calorimetry and gamma isotopic analyses (Cal/Iso) for the accountability measurement of plutonium (Pu) bearing items. In the past 15 years, the vast majority of those items measured by Cal/Iso were contained in a thin-walled convenience can enclosed in another thin-walled outer container. However, LLNL has recently begun to use DOE-STD-3013-2000 containers as well. These DOE-STD-3013-2000 containers are comprised of a stainless steel convenience can enclosed in welded stainless steel primary and secondary containers. In addition to the fact that the wall thickness of the DOE-STD-3013-2000 containers is much greater than that of other containers in our experience, the DOE-STD-3013-2000 containers appear to have larger thermal insulation characteristics. To date, we have derived Pu-mass values from Cal/Iso measurements of 74 different DOE-STD-3013-2000 containers filled with Pu-bearing oxide or mixed uranium-plutonium (U-Pu) oxide material. Both water-bath and air-bath calorimeters were used for these measurements and both use software to predict when thermal equilibrium is attained. Our experience has shown that after apparent equilibrium has been attained, at least one more complete cycle, and sometimes two or three more complete cycles, is required to gain a measure of true thermal equilibrium. Otherwise, the derived Pu-mass values are less than would be expected from a combination of previously measured Pu-bearing items and would contribute to increased loss in our inventory difference determinations. Conclusions and recommendations drawn from LLNL experience with measurements of Pu mass in Pu-bearing oxide or mixed U-Pu oxide in DOE-STD-3013-2000 containers using the Cal/Iso technique are included.

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Introduction

Lawrence Livermore National Laboratory (LLNL) routinely uses calorimetry and gamma isotopic analyses (Cal/Iso) for the accountability measurement of plutonium (Pu) -bearing items. LLNL has derived Pu-mass values from Cal/Iso measurements for seventy-four different DOE-STD-3013-2000 containers filled with Pu metal or Pu-bearing oxide or mixed uranium-plutonium (U-Pu) oxide material. Both water-bath and air-bath calorimeters were used for these measurements and both use software to predict when thermal equilibrium is attained.

The Cal/Iso measurements of DOE-STD-3013-2000 containers started in June 2001. The items that went into the 3013 containers had previous measurements before they were loaded. Once the items were loaded into the 3013 containers they were scheduled for measurement. Each 3013 container was then measured either in an air-bath calorimeter or a water-bath calorimeter and finally measured in a gamma isotopic counter. During this measurement process, the majority of the 3013 container contents measured less than the book weight. To discover the source for this discrepancy, the expected isotopic content was computed using the combined isotopic values based on previous isotopic measurements for each item going into the 3013 container in question. Comparison of the combined isotopic values with those from the current isotopic measurement indicated that the current isotopic measurement was generally accurate. Therefore, the calorimeter measurements were apparently not at true equilibrium when the computer software running the calorimeter indicated equilibrium had been reached. A determination was made that the 3013 containers needed to be measured longer to gain true equilibrium. In order to accomplish this, the 3013 container was placed into a calorimeter and measured to apparent completion. The analysis was then restarted without removing the 3013 container from the calorimeter. The data was then reviewed and it was determined that a significant difference was noted between the first and second calorimeter measurements. This process was repeated for each 3013 container as it was received. Suspecting that even this second measurement might not represent true equilibrium, each 3013 container measured as described above, was remeasured a third time, and even a fourth time, if necessary, if it did not appear equilibrated. Also, additional measurements were performed, as time permitted, for each early 3013 containers when the differences between book and first measurement was unusually large.

Results

Since June 2001, a total of seventy-four DOE-STD-3013-2000 containers have been measured with Cal/Iso. A database was established after a distinct pattern of low measurements with regard to the book mass was discovered. The database consisted of the book mass assigned at the time of processing, the first measured mass with measured isotopic content, the first measured mass with combined isotopic content, and the final measured mass with measured isotopic content. Forty-eight of the seventy-four 3013 containers were remeasured in a calorimeter, as described above (actually 49 were remeasured, but no first measured value was obtained for one of the 3013 containers since it had been preheated for a week and was considered to be a final equilibrated value.). The designation remeasured is referred to herein as applying to all later 3013

containers, as well as the early 3013 containers that were remeasured. Forty-four of the forty-nine 3013 containers showed an increase in mass compared to the first measurement. The largest gain being about 2.2%, although a number of remeasured gains were greater than one percent. Five of the 3013 containers showed losses in mass after remeasurement that were 0.09%, 0.04%, 0.013, 0.04%, and 0.22%. The magnitude of the first four differences indicates that the first measurement represents a thermally equilibrated one as the remeasured values are well within expected statistical fluctuations. The last container had a large ^{242}Pu content, and this may account for the larger value, although this difference is consistent with expected statistical fluctuations at equilibrium..

Two of the 3013 containers had Pu metal while the other seventy-two 3013 containers held Pu-bearing oxide or mixed U-Pu oxide material. Roughly half of the 3013 containers held weapons grade material. The other half contained fuels grade material, other non-weapons grade material with increased values of individual isotopes of plutonium or americium, or Pu-bearing material with considerable quantities of uranium. These latter materials also presented problems in determining isotopic values from gamma isotopic measurements because of possible lack of homogeneity (individual batches introduced into a 3013 container did not necessarily have comparable isotopic content) even though a homogenization effort had been attempted. A few items were measured in the Neutron Multiplicity Counter (NMC) to help establish the percent of the ^{240}Pu isotope. In such cases, all or part of the isotopic quantities were established using the combined isotopic values or the NMC. Twelve of the 3013 containers required such a technique for determining isotopic content.

Figure 1 shows the cumulative number of residuals vs. residual (difference between Cal/Iso and NMC/Iso divided by the standard deviation) results for the first measurements of the forty-eight 3013 containers having final remeasured values.

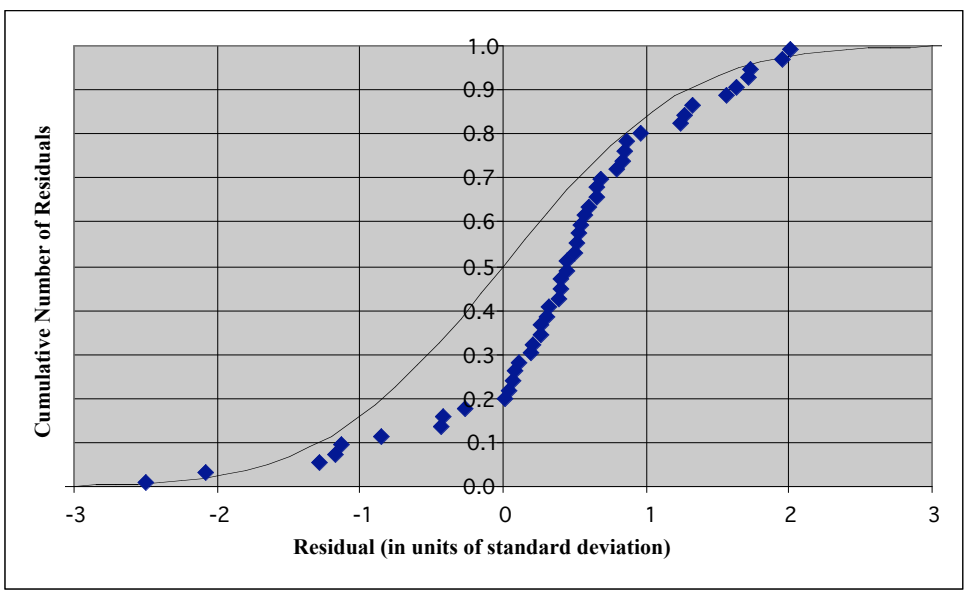

Figure 1: Solid curve is the cumulative normal distribution. The cumulative number of residuals vs. mass difference residual from the first measurement on 3013 containers (diamonds).

The solid curve is the cumulative distribution expected from normally distributed measurement values. It is observed that the measured data points do not agree very well with the normal curve. This corresponds to a bias of about 690 grams of apparent mass loss.

Figure 2 shows the cumulative number of residuals vs. residual results for the final measurements of the forty-eight 3013 containers considered in Figure 1. Again the solid curve is the cumulative distribution expected from normally distributed measurement values. The data points appear to be approximately normally distributed in relation to the solid curve. This bias corresponds to about 150 grams of apparent mass loss. Therefore, the cumulative plutonium mass gain associated with remeasurement is about 540 grams.

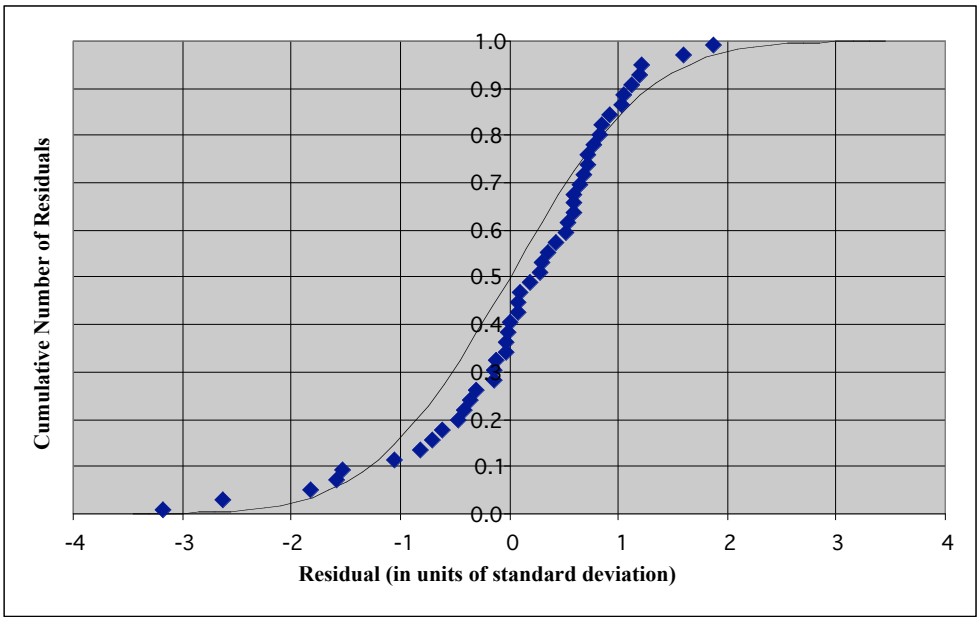

Figure 2: Solid curve is the cumulative normal distribution. The cumulative number of residuals vs. mass difference residual from the final measurement on 3013 containers (diamonds).

Twenty-five of the original 3013 containers measured just once were not remeasured. The reason for this was, in part, the need to adhere to ALARA requirements to minimize personnel exposure to high radiation material. Therefore, a decision was made to remeasure only 3013 containers with a substantial mass difference of approximately 20 grams or more. If these twenty-five 3013 containers had also been remeasured this might have reduced the apparent measurement bias below the 150 grams of apparent mass loss.

Discussion

LLNL routinely uses Cal/Iso for the accountability measurement of Pu-bearing items. In the past 15 years, the vast majority of those items measured by Cal/Iso were contained in a thin-walled inner can enclosed within a polyvinyl-chloride bag inside a polyethylene bag (several types are possible), which was then put into another thin-walled outer can. The sample/double-can arrangement was then placed in a calorimeter can with aluminum foil balls filling the void. The inner can has a wall thickness of about 0.2 mm with an

outer can of 0.3 mm wall thickness. There is typically a rather tight fit between the inner-can/polymer-bags and the outer can. This sample/double-can arrangement situation is generally true for the accountability measurements made at other DOE laboratories. The software developed for controlling calorimeter measurements essentially assumes that Pu-bearing unknowns are in this container configuration, so the software indicates that thermal equilibrium is achieved when the rate of change of temperature reaches some acceptably small value.

Each DOE-STD-3013-2000 container consists of a screw-lid stainless-steel convenience can enclosed in a welded stainless-steel primary within a welded stainless-steel secondary container. The wall thickness of the 3013 convenience can and primary and secondary containers is 1.0, 1.5 and 3.0 mm, respectively, which is much greater than that of other containers in our experience. The average gap between the convenience can and primary container, and primary and secondary containers is about 1 mm for both, each with helium at approximately atmospheric pressure and just above one atmosphere, respectively. Based on the measurements described earlier in this paper, the DOE-STD-3013-2000 containers with Pu-bearing material appear to have larger thermal insulation characteristics than do typical inner-can/outer-can arrangements. As such, when the software indicates thermal equilibrium has been achieved, that may not necessarily be the case. It appears that thermal equilibrium for 3013 containers should be determined when the rate of change of temperature reaches an even smaller value than current software employs. It is instructive to investigate the heat transfer processes that take place in the two cases. Heat transfer takes place by thermal conduction in both types of sample/container arrangements since there is not enough space available for convection cells to form.

In both cases the multiple-container arrangements are placed inside a calorimeter can with aluminum foil balls filling the void. Because of this the heat transfer, in both cases, from the outer container of each multiple-container arrangement and the calorimeter can walls is assumed to be essentially the same. In addition, in both cases the sample-bearing container walls (inner can or convenience can) are in thermal equilibrium with the Pu-bearing material within. The difference arises because of heat transfer in the spaces between containers. The entire secondary 3013-container wall (including top and bottom) is at approximately the same temperature because the heat conductivity of the wall material (stainless steel) is large compared to the heat conductivity of the helium gas. The entire outer-can wall for the typical inner-can/outer-can arrangement is also at approximately the same temperature since the thermal conductivity of regular carbon steel is much larger than that of polymer/air (the thermal conductivity of regular carbon steel is larger than that of stainless steel by a factor of about two).

For the typical inner-can/outer-can case the heat transfer through the approximately 3 mm gap between the two cans occupied by the polymer bags and air (or possibly argon or nitrogen) at atmospheric pressure will be predominantly by way of the polymer material since that heat conductivity is about an order of magnitude larger than that of air (or argon or nitrogen.) For the 3013 container, the 1 mm gap regions between the convenience can and primary container, and primary and secondary containers is filled with approximately one atmosphere of helium gas. The lower heat transfer through these two gaps for the 3013 container must be due to the lower effective thermal conductivity

of the helium fill relative to that of the gap filled with polymer/air for a typical inner-can/outer-can arrangement. Other than by measurement, establishing an accurate effective heat conductivity for this gap would be difficult. Yet the effective thermal conductivity of the two helium gaps is estimated to be less than about one-half of the effective thermal conductivity of the polymer/air gap.

Conclusions and Recommendations

The results presented in this paper show that calorimetry measurements of 3013 containers with Pu-bearing material must be performed over a sufficient time period that thermal equilibrium is attained, for otherwise, a distinct reduction in the measured Pu mass can occur. This may require the sequential remeasurement of a 3013 container without removal of the container from the calorimeter, from two to four separate measurement time sequences. This situation arises because of a reduced heat transfer between the primary and secondary-containers for 3013 containers. The reduction in heat transfer has given spurious equilibrium outputs. A series of forty-eight 3013 containers measured for only a single measurement time sequence in a calorimeter gave a mass loss bias of 690 g. When a number of 3013 containers are involved the cumulative mass difference can represent a substantial apparent mass loss and can have a significant effect on the inventory difference for a given time period. When the same forty-eight 3013 containers had multiple sequential measurements the bias was reduced to 150 g. This remeasurement has significantly reduced the apparent mass loss in these 3013 containers.

A recommendation is that all 3013 containers or similar containers be left in a calorimeter and measured at least twice, and possibly three or four times, to ensure equilibrium and to reduce the handling of the highly radioactive material. Preheating the 3013 container for at least twelve hours would help reduce the measurement time necessary and ensure equilibrium. In addition, the isotopic measurement of a sample must also be carefully examined to avoid the introduction of additional mass errors due to possible sample inhomogeneities and the presence of non-weapons grade Pu-bearing materials.

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