PLUTONIUM WORKING REFERENCE MATERIALS FOR THE NDA PDP PROGRAM

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ABSTRACT

Sixty-three QC standards, termed Working Reference Materials (WRMs) are being fabricated at Los Alamos for the Non-destructive Waste Assay Performance Development Plan. The WRMs require Pu and Am distributed uniformly in a low density matrix. A silicone rubber matrix initially specified has been changed to a packed, diatomaceous earth (DE) matrix to facilitate Pu-DE uniformity and minimize gas generation and WRM pressurization. Uniformity and separation stability was demonstrated with iron powder-DE mixtures. To meet the rigorous quality objectives on the mass of Pu and Am for each WRM, a uniform, stable batch of PuO2 with relatively high Am-241 content was prepared by blending, calcining, and screening. Multiple sample analyses demonstrated the PuO2 to be highly uniform and established that tight Pu and Am assay and Pu isotopic analysis precision requirements were met. Test blends were prepared and tested to successfully demonstrate Pu uniformity, freedom from PuO2 clumping, and acceptable alpha-neutron generation rates. Blends of PuO2-DE were prepared individually for each WRM; all 63 blends have been prepared. After loading and packing the blends into zircalloy cylinders, the air atmosphere will be replaced with helium and end caps inserted and welded. Following decontamination and leak checking, the cylinders will be loaded into secondary zircalloy cylinders and sealed with welded end caps.

INTRODUCTION

The performance of NDA waste measurement systems used for analysis of waste materials destined for disposal at WIPP will be tested using blind standards to meet the requirements set forth in the TRU Waste Characterization Program Quality Assurance Program Plan. The standards are designated as Working Reference Material (WRMs). Design and quality objective specifications for the WRMs were established by a team of scientists representing NDA measurement and measurement system design personnel from several DOE sites. The Los Alamos National Laboratory was selected to produce the 63 WRMs.

The WRMs were designed to provide exact quantities of Pu and Am-241 uniformly distributed in a low density matrix material. The WRMs will be prepared in three sets: one containing ~20-40 mg Pu, one containing ~200-400 mg Pu and one set containing ~2-4 g Pu. Exact quantities are not revealed to ensure objective "blind" performance testing of the waste measurement systems. The WRM matrix will be contained welded zirconium cylinders designed to allow contamination free, safe handling and minimum interference to a variety of NDA measurement systems. Silicone rubber was originally suggested as the matrix material.

Preliminary Evaluations

Initial discussions at Los Alamos centered on some problems that might occur if the silicone rubber matrix was used. Previous attempts to blend PuO2 with silicone 'caulking' material showed that the viscous silicone did not 'wet' the PuO2 powder making mixing very difficult. The PuO2 powder remained as clusters in the silicone despite considerable effort to uniformly disperse the powder. Secondly, since silicone rubber typically has a hydrogen content almost equal to that of carbon-based organic polymers, radiolysis from alpha

particles emitted from Pu and Am-241 would lead to hydrogen gas formation pressurizing the zircalloy containment to several atmospheres in the first year. Thirdly, the commercial silicone rubbers have a density >1, somewhat greater than the desired matrix density.

Diatomaceous earth, an amorphous silica material, was suggested as a substitute matrix. Los Alamos had previously prepared several sets of Pu and U standards with this low-density, free flowing, crystalline, fine powder for gamma-based NDA instruments. There were, however, three concerns about this substitute matrix material:

a. would the PuO2 separate from the DE with handling,
b. would the finely divided PuO2 uniformly distributed in this silica matrix introduce an unacceptably high alpha-neutron flux, and
c. would the PuO2 tend to clump or cluster during blending with DE?

Separation of PuO2 from the DE matrix had been addressed in previously prepared gamma standards by providing adequate void space in the container to allow the user to re-mix the materials prior to usage. This practice does not provide a well defined configuration because the PuO2-DE powder can 'pack' thereby changing the vertical height of the matrix by 25-30%. An alternative approach is to pack the PuO2-DE thereby restricting movement and separation of the PuO2. To demonstrate the stability of a packed mixture, a mixture of finely divided iron powder and DE was prepared by thoroughly stirring the powder mixture. The mixed powder was then placed into a glass graduated cylinder. The material was 'tap' packed', i.e. as the material was added incrementally, the container was thrust downward onto a bench top thereby packing the material during loading. This operation produced a stable fill height indicating that further movement of particles within the packed column was unlikely. The glass cylinder was then measured in a

segmented gamma scanner (SGS) where a 400 keV gamma ray beam passed through the packed column at one inch intervals. The iron powder, and to a lessor degree the DE, adsorbed about 25% of the gamma ray beam. That fraction of the beam transmitted through the column was measured and provides a measure of uniformity of the iron powder. After initial SGS measurements, the glass cylinder was vigorously vibrated with a laboratory "vortex" mixer for 12 hours and the cylinder re-measured with the SGS. The results of the before and after vibration SGS measurements are listed in Table 1.

Table 1.

SGS Transmission Measurements on a Fe Powder-Diatomaceous Earth Column Before and After Vibration

Segment	Before Vibration		After Vibration	
Number	%Trans.	σ	%Trans.	σ
1	0.778	0.021	0.707	0.022
2	0.770	0.021	0.738	0.022
3	0.788	0.021	0.736	0.022
4	0.798	0.021	0.754	0.023
5	0.776	0.021	0.729	0.022
6	0.774	0.021	0.741	0.022
7	0.751	0.021	0.755	0.022
	x = 0.776		x = 0.737	

The Table 1 data indicates no statistical difference in the 400 keV gamma ray transmission values for the seven packed column segments before vibration. The After Vibration transmission values indicate a possible lowering of the transmission (increased density) of the packed column and possibly a significant change in the top segment. During vibration, we noticed movement in the top segment which may have allowed an upward movement of the more dense iron particles. The WRM design requires essentially zero space above the matrix hence change in matrix density or uniformity are unlikely.

To address concerns about alpha-neutron yields and PuO2 clumping, a blend was prepared using the highest PuO2/DE ratio specified for the WRMs. This blend was prepared using WRM preparation procedures and equipment. The blend was then measured in a Shuffler neutron assay instrument to determine the total neutron flux. Also, a PuO2 sample containing the same quantity of PuO2 was measured in the same instrument. The total neutron flux ratio of the PuO2-DE blend to the PuO2 was 1.37 and considered quite acceptable for the WRMs because this level of added random neutrons flux will not appreciably degrade the neutron-based assay systems precision.

A sample of the PuO2-DE blend was examined under a light microscope. Under appropriate illumination, the PuO2 particles were readily distinguishable in the translucent DE matrix. The photomicrograph were processed via a image scanner and major and minor axis dimensions determined. The particle size distribution of PuO2 in the PuO2 used to prepare the blend was determined in a scanning laser particle size analyzer. Table 2 compares the PuO2 particle size distribution in the blend with that of the PuO2 starting material.

Table 2. PuO2 Particle Size in Blend and In PuO2 Starting Material

Range,μ:	5-15	16-25	26-35	36-45	46-55	56-65	65-75
Blend,%:	38	27	20	9	2	2	2
PuO2 [a],%	25	20	9	10	6	5	4

a. The more extensive particle size analyzer showed 14 % particles smaller than 5 microns and 8% larger than 75 microns.

It appears that the blending operation reduced the PuO2 particle size hence there is no indication of 'clumping' which might introduce bias to measurement methods.

Meeting the WRM Quality Objectives

The Quality Objectives of the WRM production task are met through careful planning, frequent and effective communication, knowledgeable inspection, selection of qualified personnel, usage of quality materials (including NIST/NBS standards), frequent and formal data review, documentation and records management. Our success in meeting two potentially difficult technical quality objectives are described.

The WRM contained alpha activity must be quantified with maximum uncertainty at the 95% confidence level of 0.5% for WRMs containing >50 mg Pu and 1% for WRMs containing <50 mg Pu. To meet this objective, all those components contributing to the uncertainty of the Pu and Am quantities in each WRM were identified and controlled. Table 3 lists the components contributing to the alpha activity quantification and their determined or estimated random uncertainty.

Table 3. Components to Alpha Activity Quantification and their random uncertainties

Component	No. of samples	mean value	random uncertainty, relative percent @ 1σ
PuO2 Homogeneity	5	see Pu & Am assay and note [a] below	
PuO2 Assay	5	87.82%	0.03%
Am Assay	5	768 ppm	0.01% [b]
Pu Isotopic, 239Pu	5	93.76 %	0.09%
Weighing	13	NA	0.16%
Transfer loss, & spillage	21	<<1%	est.<0.1%
Dusting	2	<<1%	est.<0.05%
Isotope specific alpha activity	NA	"Best" literature values [c]	

a. Because portions of the single PuO2 batch are weighed out for each individual WRM, the most meaningful evaluation of the homogeneity is through the consistency of Pu and Am concentration in the PuO2. Five samples taken from different regions within the PuO2 batch were individually analyzed for weight percent Pu and Am and for Pu isotopic composition. Note that the homogeneity of the PuO2-DE blend is not a factor in the alpha activity determination because each WRM is prepared from its own unique PuO2-DE blend.

b. While the random uncertainty on the Am measurement was 0.16% (1σ), the alpha contribution to the total alpha activity is only ~5% hence the effective random error is 0.01% at 1σ.

c. Note that the alpha specific activity for each alpha emitting isotope does not contribute to the random uncertainty because a "best" literature value will be used and can be updated when more robust values for isotope half-lives are forthcoming in the future.

The largest single contributor to the random uncertainty is the weighing operation. This error term has the largest effect on those WRMs requiring the smallest mass of PuO2 weighed out. The relative uncertainty for weighing that is listed in Table 3, is the "worst case" error corresponding to WRMs containing <50 mg Pu.

The overall random uncertainty calculated by summing the variance (σ^2) of the components in Table 3 is 0.21% or ~0.42% at 95% confidence, well within the design quality objective of 0.5% at 95% confidence.

The second technical quality objective that had to be met was a blend Pu homogeneity or uniformity as follows:

a. 20-40 mg WRM: +/-30% of mean concentration for any given 20 cm^3 volume.
b. 200-300 mg WRM: +/-15% of mean concentration for any given 20 cm^3 volume.
c. 2-4 g WRM: +/-10% of mean concentration for any given 20 cm^3 volume.

To evaluate our ability to meet these objectives, the Pu content had to be evaluated for 20 cm^3 samples of the blends. To take multiple samples of the blends and perform traditional dissolution and destructive assays would have proven costly (~$40K) and generated considerable waste. Preliminary experiments showed that we could perform a much more cost-effective evaluation by counting the prolific 59.6 keV 241Am gamma ray contained in 20 cm^3 of the "leanest" blend with a counting precision of ~1%. Key to this type of nondestructive measurement is the careful control of the "geometry" of the container housing the blend sample and the blend material within the container. The sample containers were positioned 20.0 cm from the gamma detector face and the sample center of mass controlled to within +/- 0.5 mm. Since the Am-241 is a daughter product of the sample Pu (Pu-241 isotope)and thereby an integral part of the PuO2 particles, the Am-241 measurement provides an indirect measurement of the PuO2 particle homogeneity.

Six, 20 cm^3 samples were taken from each of the three ranges of Pu-DE blend, weighed, and the Am-241 gamma peak counted. If the count rate was excessive (counter dead time >50%), a cadmium filter was used to decrease the count rate. The counting results, expressed as 10 minute counts per gram of Blend, are listed in Table 4.

Table 4. Blend Homogeneity Assessment via Am-241 Gamma Counting.

Blend Type	Mean 59.6 Peak Area	Peak Area Unc., 1 σ	1 %RSD
20-40 mg Pu	27863	439	1.58
200-400 mg Pu	13252	66	0.50
2-4 g Pu	14726	84	0.57

The homogeneity assessments show that the blend uniformity objectives were clearly met.

The Blends will be transferred into zircalloy cylinders using precautions to minimize and recover any spillage. Each incremental addition of blend material will be tap-packed to ensure a uniformly packed matrix and to achieve a fill height within 1.25 cm +/- 1 mm of the top of the cylinder. A disk graphite felt will be placed on top of the packed matrix to restrict any movement of the matrix. Next the cylinders will be transferred to an airlock and the airlock evacuated and back-filled with helium. The cylinders will then be brought into a helium atmosphere glovebox, end caps inserted and welded.

After welding the cylinders will be decontaminated, helium leak checked, inserted into a close-fitting secondary zirconium cylinder, then an end cap will be inserted and welded. Finally, the WRM Pu content and matrix Pu uniformity will be verified by gamma counting one inch segments. This final check will not be so robust as the measurements performed on the blend preparations but serves primarily to verify that no mistakes were made during the loading and welding operations.

SCHEDULE AND DELIVERY

Thanks to frequent and enthusiastic discussions between the Los Alamos fabrication team, the WRM design team, and LMIT management, the WRM production proceeded rapidly and on schedule through the preparation of the 63 blends. We have all been disappointed at unexpected delays in the delivery of the zircalloy cylinders. Delivery of the zircalloy cylinders are expected in late October and the loading, welding, inspection, and verification operations should be completed within 2 weeks after receipt of the zircalloy cylinders. Shipment to the receiving sites will begin in mid-November with sites receiving the WRMs during November and early December.

SUMMARY AND CONCLUSION

Sixty three WRMs are being prepared from PuO2-DE blends. All Quality Objectives have been met to ensure the WRMs will contain NIST traceable, accurately and precisely defined quantities of Pu and Am. Frequent discussions between the fabrication team and the WRM designers and Project managers has allowed the WRM blend preparation to proceed efficiently on a tight schedule. Delays in delivery of the zircalloy containers have delayed blend loading operations and has extended delivery dates of the WRMs from October to late November-early December, 1995.

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