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RADIOMETRIC MEASUREMENTS ON THE FABRICATION OF NON-DESTRUCTIVE ASSAY STANDARDS FOR WIPP-PERFORMANCE DEMONSTRATION PROGRAM

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The Inorganic Elemental Analysis Group of LANL has prepared several different sets of working reference materials (WRMs). These WRMs are prepared by blending quantities of nuclear materials (plutonium, americium, and enriched uranium) with diatomaceous earth. The blends are encapsulated in stainless steel cylinders. These WRMs are being measured as blind controls in neutron and gamma based non-destructive assay (NDA) instruments. Radiometric measurements on the blending homogeneity and verification on a set of sixty three plutonium based WRMs are discussed in this paper.

INTRODUCTION

Plutonium based non-destructive assay (NDA) standards, called working reference materials (WRMs) are being provided as part of the Waste Isolation Pilot Plant (WIPP) Performance Demonstration Program (PDP) which is sponsored by the DOE Carlsbad Area Office. This program is designed to help ensure compliance with quality assurance objectives identified in the Transuranic Waste Characterization Quality Assurance Program Plan for the WIPP[1,2]. The NDA WRMs are used to evaluate the performances of various gamma and neutron based NDA systems. These instrumentation included segmented gamma scan (SGS), passive and active neutron interrogation (PAN) systems, tomographic gamma scanner (TGS), and ^{252}Cf Neutron Shuffler systems.

The NDA PDP program is managed by the Idaho Nuclear Engineering Laboratory (INEL) currently operated by Lockeed Martin Idaho Technologies Company (LMITCO). In FY 96, the Inorganic Elemental Analysis (CST-8) group of the Los Alamos National Laboratory

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(LANL) fabricated sixty-three Phase I PDP WRMs for LMITCO. These NDA WRMs were prepared from a well-characterized plutonium oxide (PuO_2) which was uniformly mixed with diatomaceous earth (DE) matrix and encapsulated in a dual stainless steel cylinder configuration. The quality objectives of the WRM fabrication included the uncertainty of the contained alpha activity must be within ± 0.5 % at 95 % confidence level; the WRMs must be traceable to a national certifying laboratory or agency (e.g., the New Brunswick Laboratory, NBL; or National Institute of Standards and Technology, NIST); the uniformity of blending and homogeneity within each WRM should be ±30 % for the 20-40 mg Pu range, ± 15 % for the 200-400 mg Pu range, and ± 10 % for the 2-4 g Pu range.

In order to meet the stringent quality objectives of these WRMs, a batch of PuO_2 powder was thoroughly conditioned and characterized before being used as the nuclear component during the fabrication. The CST-8 Radiochemistry team provided the ^{241}Am, ^{244}Cm, and ^{252}Cf characterization on this PuO_2 powder. The other radiometric supports including the uniformity of PuO_2-DE blending, correction for the retention of PuO_2-DE mixture in the waste item, the uniformity within each WRM, and the final Pu verification measurements on the WRMs are discussed in this paper.

MATERIALS AND METHODS

A batch of well-characterized weapon grade PuO_2 sample was prepared by the LANL Plutonium Facility specifically for the production of NDA WRMs. This batch of PuO_2 powder was blended, calcined (between 900°C and 960°C), pulverized, and screened to generate a stable (low surface area) material.

Characterization of Pu Oxide. Five aliquots of samples were taken from a batch of 120 g of PuO_2 material. The samplings represented different vertical and horizontal regions of the PuO_2 batch in the bottle. Plutonium assay (by coulometric titration), Pu isotopic distribution (by mass spectrometry), and ^{241}Am assay (by mass spectrometry and radiochemistry) were performed on these five aliquots of PuO_2 sample. Duplicate or replicate analyses were done on each sample aliquot. Particle size distribution, metallic impurities (by DC Arc Emission and ICP-MS), and anion analysis (by ion chromatography) of PuO_2 powder were performed on three aliquots of the batch. Alpha spectroscopy was used to evaluate ^{244}Cm and ^{252}Cf level in the PuO_2 batch. Analyses on all radionuclides and most impurities were either traceable to the NBL or NIST via their certified reference materials (CRMs) or standard reference materials (SRMs). The analytical analysis results of this PuO_2 material are proprietary information and will not be included in this paper.

Homogeneity of Blending. PuO_2-diatomaceous earth blends were individually prepared for each WRM. Between 129 to 140 g of DE were weighed into a 1-L polyethylene, wide mouth blending bottle. PuO_2 powder was weighed to the nearest 0.02 mg and transferred quantitatively into the blending bottle. This blending bottle was sealed, secured in the Turbula™ blender, and blended for 20 minutes. In order to meet the blending quality objectives, three mass ranges of PuO_2-DE blend mixtures were evaluated for homogeneity. Six, approximately 8.3 g blend mixture samples were taken from different portions of each blend and packed into 30-mL flat bottom high precision plastic vials. The blend mixture was filled to a fixed height (± 0.5 mm) for a total volume of ~ 20 cm^3. Each blend sample was weighed to nearest 0.02 mg. Each bottle was position in a fixed geometry, 15 cm above a high purity germanium detector. The counts of

the 59.5-keV ^{241}Am peak were accumulated for sufficient time to obtain counting statistics error of $\leq$ 0.5 %. The homogeneity of each PuO_2-DE blend mixture was estimated from the consistency of the six samples at 59.5 keV ^{241}Am peak area per unit mass of the sample.

Preparation of WRM. After three mass ranges of the blends were proven to be homogeneous and met the uniformity quality objective, the blend for each WRM was prepared individually. While loading the PuO_2-DE blend into the stainless steel cylinder for each WRM, extra care was taken to minimize the loss and spillage of the blend mixture. Prior to loading each WRM, the glovebox was wiped down with a damped cloth to prevent cross contamination from the dusting of each PuO_2-DE mixture. A clean brown paper (30 x 30 cm) was placed on the glovebox surface while packing the blend into the cylinder. Any spills of the blend mixture were added back into the cylinder. All the paper tissues, cotton tips, and paper funnel used during the blending and transferring operations were placed inside of the emptied blending bottle. These materials became the waste item for each WRM.

Waste Item Measurement. The amount of the PuO_2-DE mixture left in the waste item for each WRM was determined by a fixed geometry non-destructive gamma-ray analysis. Since the concentration of ^{241}Am in the PuO_2 sample was accurately determined by both mass spectrometry and radiochemistry, the amount of PuO_2 left in the waste item was determined via the measurements of ^{241}Am gamma rays at 59.5 keV.

A standard was prepared closely matching the waste items. This standard item included a clean blending bottle, a clean brown paper, cotton tips, paper funnel, and paper tissues. Four pieces of cloth swipes spiked with the NIST traceable ^{241}Am standardized solution were taped symmetrically around inside of this standard blending bottle. The waste item standard contained

a total of 322.68 nCi or 94.13 ng of ^{241}Am. The uncertainty of the total activity in this standard was 0.50 % at 95 % CL which included the uncertainty in the ^{241}Am solution concentration and in aliquoting this solution. The amount of ^{241}Am in each of the waste items was determined by comparative method. The amount of ^{241}Am activity in the waste item was calculated from the count rate ratio at 59.5-keV gamma peak for the waste item and the standard. The count time for each waste item was 20 minutes and the distance to the detector was 45 cm.

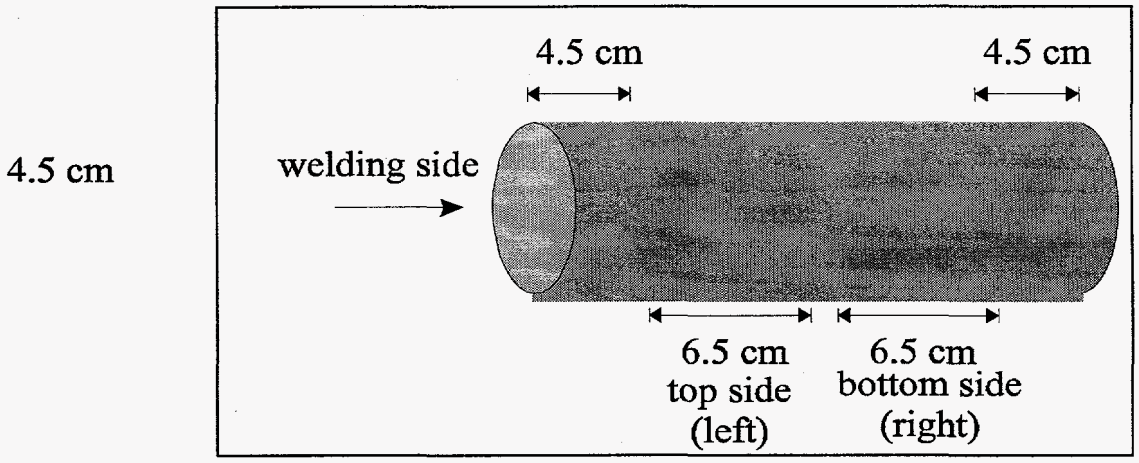
Welding of the Assembly. After the blending mixture was loaded to the inner layer of the stainless steel tube, a graphite felt frit was carefully inserted and gently pressed down onto the surface of the powder. Then this loaded WRM was transferred to an inert gas welding box where a stainless steel end cap was inserted and welded in place. These WRMs were carefully decontaminated, helium leak checked and inserted into a second stainless steel tube with welded endcaps.

Verification Measurements of the WRM. Each WRM was subjected to collimated gamma-ray intensity measurements focused on two segments of the cylinder. The purpose of these measurements was to determine the vertical homogeneity within the length of each WRM after it was filled with PuO_2-DE blend. Figure I illustrated the segments of WRM being verified. The WRM cylinder was placed horizontally inside of the lead cage with a 6.5 cm wide aperture. The detector distance was 40 cm from the lead cage. Each side of WRM (left or right) was counted for 300 to 1200 seconds depending on the amount of Pu in each WRM. The net area of the ^{241}Am 59.5-keV, the ^{239}Pu 129-keV, and the ^{239}Pu 414-keV gamma-ray peaks were recorded.

^{239}Pu Content Verification. In order to verify the amount of plutonium in each WRM, the normalized count rate (counts per minute per g of Pu in each WRM) in the ^{239}Pu gamma ray peaks were evaluated. The WRM was placed in a fixture and counted at a fixed 45 cm distance

from a collimated Ge(Li) gamma-ray detector. Gamma-ray peak areas at 129, 208, 375, and 414 keV were integrated. Three mass ranges of PuO_2-DE blends were evaluated.

Figure I. WRM Verification



RESULTS AND DISCUSSION

Analytical Characterization of PuO_2. To preserve the blind control usage of the WRMs, the analytical characterization results of PuO_2 materials for the fabrication of NDA WRMs cannot be disclosed in this paper. Radiochemistry team performed several analysis on this PuO_2 material. Gamma-ray analysis of ^{241}Am was performed to confirm the ^{241}Am analysis value obtained by isotope-dilution mass spectrometry. There was a good agreement (within 0.6 %) between these two analysis methods. The levels of ^{244}Cm and ^{252}Cf in the PuO_2 sample were determined by alpha spectrometry. ^{244}Cm and ^{252}Cf were the radionuclide impurity of concern when performing neutron based non-destructive measurements. Five aliquots of sample were verified by the alpha spectrometry. No alpha activities were detected above 5.7 to 6.5 MeV energy region. Based on the background of this energy region (total counts in 3600 seconds were zero), assumed minimum detectable activity (5 counts in 3600 seconds if ^{244}Cm or ^{252}Cf

was present in the sample), and the ratio to the peak area at 5.155 MeV (^{239,240}Pu), a conservative estimate was made based on the half-life of these isotopes. The level of ^{244}Cm was < 0.5 μg/g Pu, and ^{252}Cf was < 0.1 μg/g Pu.

Alpha Specific Activity of the PuO_2 Sample. The alpha specific activity was calculated using the Pu assay, isotopic composition of PuO_2, the half-life of each isotope[3,4], and the % of alpha emission for each isotope. The total alpha activity in each WRM was calculated based on the specific activity of PuO_2 multiplied the amount of PuO_2 in the WRM. The uncertainty of PuO_2 specific activity which includes the uncertainties of isotopic specific activity and isotopic abundance was ± 0.32 % at 95% CL. The biggest contributed factor for the uncertainty was ^{238}Pu isotope. This specific activity value of the PuO_2 sample was later verified by the Radiochemistry team through the preparation of diluted PuO_2 solutions. All the aliquot and dilution steps were performed gravimetrically. The liquid scintillation counting was used to determine the total alpha activity. The final result was within 0.04 % of expected value[5].

Homogeneity of Blending. The measurement results of three different blend mixtures are given in Table I. The homogeneity of the blending mixtures was excellent. The data showed that a 20-minute blending was adequate for all the PuO_2-DE mixtures. Therefore all other blends at these three weight ranges were blended for 20 minutes on the Turbula™ blender.

Waste Item Measurements. The center of waste items and waste item standard were aligned and positioned carefully with the center of the detector during measurements. The waste item standard was counted twice each day during 7-day measurements. A total of eleven 20-minute counts were taken on the standard bottle. The relative standard deviation of the mean

count rate (1163 counts in 20 min.) of the waste item standard was 3.3 %. The uncertainty was contained in the background subtraction and counting error of 3.9 %.

Table I. Blend Homogeneity Test Data

Blend Mixture	^{241}Am at 59.5 keV, counts/g blend [1]		
Bottle #	20-40 mg Pu (600 seconds)	200-400 mg Pu (1000 seconds)	2000-4000 mg Pu[2] (600 seconds)
1	28399	13355	14772
2	27664	13220	14634
3	27879	13214	14798
4	27893	13214	14887
5	27139	13228	14741
6	28200	13185	14726
Average	27863	13252	14760
% deviation[3]	1.28	0.40	0.46

[1] Count time varied from 600 to 1000 seconds. The counting distance was varied for these three weight range measurements due to the detector dead time.
[2] Measurements were done with a Cd filter in front of the detector.
[3] % deviation = $t * \sigma/\sqrt{n}$ at 95 % CL.

Two waste items were evaluated for the Pu non-uniformity and position effects. The bottles were counted after placing in the different geometry (front, back, left, and right sides of the bottles facing the detector surface). The first item had an average of 855 ± 32 counts in 900 seconds, the % RSD was 3.8 %. The second item had an average of 988 ± 43 counts in 900 seconds, the % RSD was 4.4 %. From these counting data, the relative standard deviation of the geometry variations was similar to the counting precision of the waste item standard and was within the counting statistic of this count rate. Therefore no appreciable error was introduced from non-uniform Pu distribution in the waste bottle or from repositioning the waste item measurements at a 45-cm counting distance.

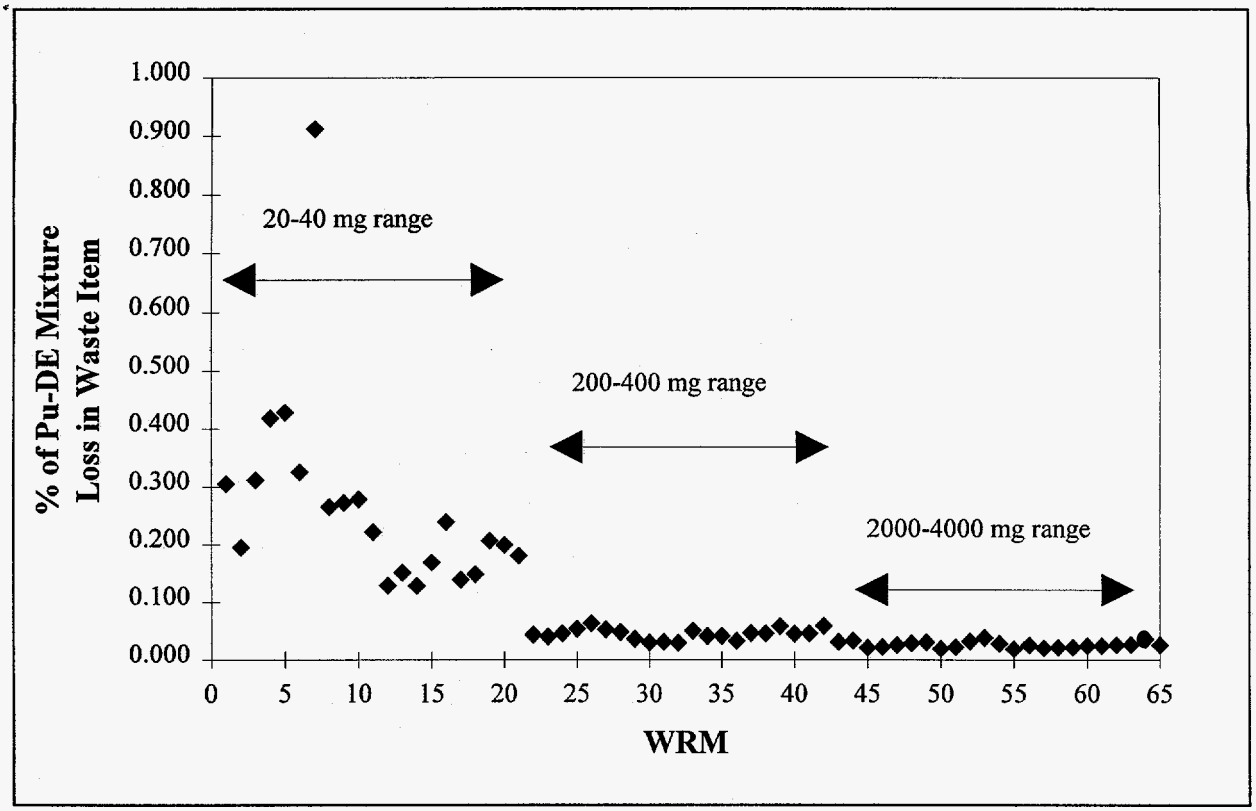
The waste items for WRM were measured at this fixed counting geometry. A total of sixty-three waste items were measured. In a 1200-second measurement, the counting statistics

ranged from 0.9 % to 10.6 % depending on the total number of counts (~ 440 to 14,000 counts). The total number of counts in each waste item was compared to the total number of counts in the waste item standard and converted to ng of ^{241}Am. The plutonium in each blend was then corrected for the amount of Pu in the waste and the net amount of Pu in each WRM calculated as follows:

$$\text{WRM Net Pu, g} = \frac{\text{g of } PuO_2 \text{ in blend}}{87.82\ \%} - \frac{\mu\text{g of Am}}{\mu\text{g Am / g Pu}}$$

With one exception, the fraction of WRM PuO_2 retained in the waste items ranged from < 0.1 % to 0.5 % (Figure II). The one exception was a WRM containing ~ 30 mg of Pu for which 0.9 % of the Pu was contained in the waste item. The uncertainty in this loss correction was < 0.1 % of total Pu at 95 % CL.

Figure II. Percent of PuO_2-DE blend left in the Waste Item.



WRM Homogeneity Measurements. The net areas of each gamma ray obtained from the left and right sides (or top and bottom segments) of each WRM were compared, and the gamma-ray ratios of these two segments at different energies were calculated. Table II gives the summary of the uniformity measurement data of three weight range WRMs. From the data summarized in Table II, the uniformity measurements of all the WRMs were well within the quality objective.

TABLE II. Uniformity Measurement Data Summary

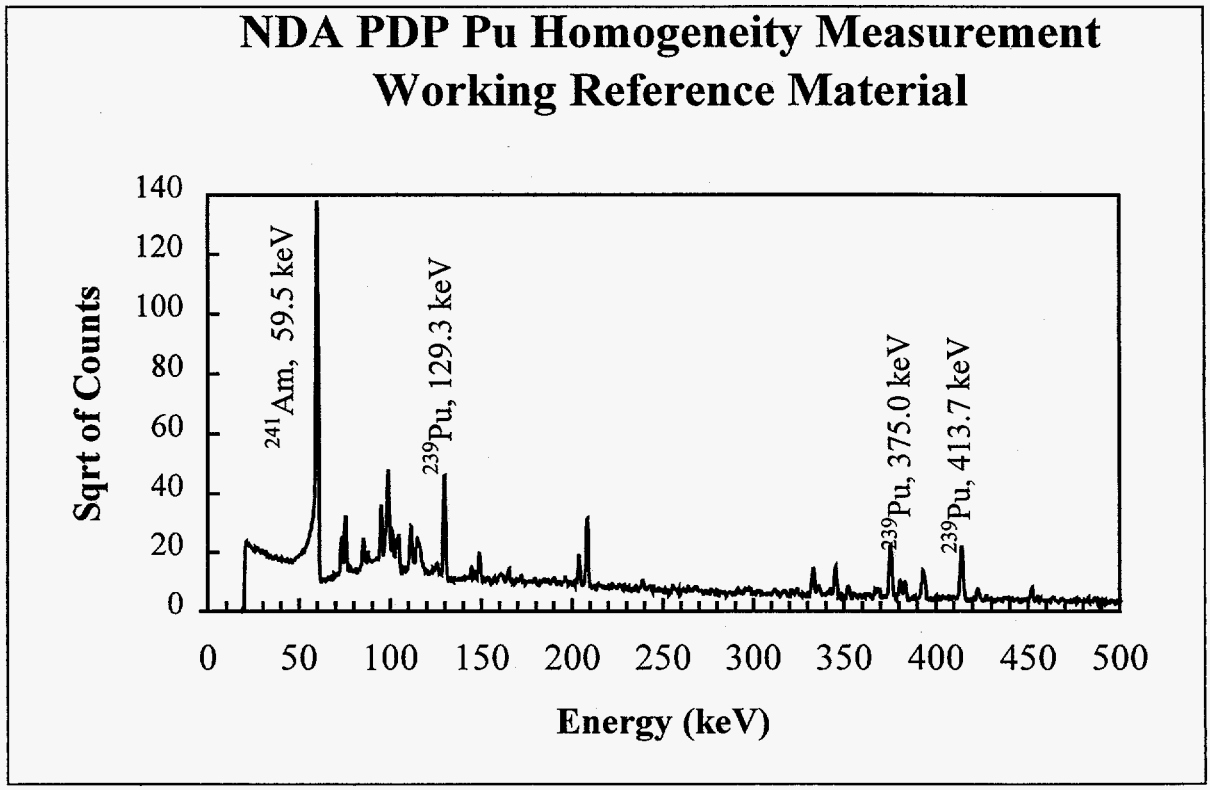
		Mean gamma ray ratio of left and right		
WRM Wt Range	Quality Objective	at 59.5 keV	at 129 keV	at 414 keV
20-40 mg Pu	± 30 %	1.04	1.04	1.06
200-400 mg Pu	± 15 %	1.02	1.05	1.05
2000-4000 mg Pu	± 10 %	0.97	0.97	0.98

^{239}Pu Verification Measurements. Figure III shows a typical gamma-ray spectrum of the WRM measurement. The ^{239}Pu gamma ray peaks (129, 208, 375, and 414-keV) obtained from the measurement were normalized with the mass of plutonium in each WRM. The purpose of these measurements was to provide a verification of the Pu content in each WRM by comparing the normalized count rate, counts per second per g of Pu (Table III).

TABLE III. The Normalized Pu Count Rate (counts per second per g of Pu) without the self-attenuation correction.

WRM / Energy	129-keV	208-keV	375-keV	414-keV
20-40 mg Pu	55.03 ± 1.70	32.88 ± 0.83	14.82 ± 0.53	12.05 ± 0.49
200-400 mg Pu	53.28 ± 0.72	32.46 ± 0.69	14.40 ± 0.18	11.65 ± 0.21
2000-4000 mg Pu	50.26 ± 0.89	32.16 ± 0.25	14.51 ± 0.21	11.81 ± 0.11

FIGURE III. A Typical Gamma-Ray Spectrum of a WRM.



From the data in Table III, the self-attenuation of gamma rays at 129 keV was appreciable. The high density (~11.46 g/cm^3) PuO_2 powder was finely dispersed in the low density (~0.4 g/cm^3) diatomaceous earth matrix. The low energy gamma rays (59.5 keV from ^{241}Am and 129 keV from ^{239}Pu) emitted from the PuO_2 material can be easily attenuated by the Pu oxide matrix itself. The normalized count rate between the highest and lowest weight range WRM was ~ 9 % difference at 129 keV and ~ 13 % at 59.5 keV. An effort to perform the attenuation correction factors (CF) on the normalized count rate was made on the calculation. The attenuation correction factor[6] for a cylinder object is

$$\mathbf{CF} = \frac{-(\pi/4) * \mathbf{lnT}}{\mathbf{1} - \mathbf{T}^{\pi/4}}$$

where T is the transmission of gamma rays, $T = I / I_o$ or $T = e^{-\mu_l D}$
I, I_o are the intensity with and without sample in place.
μ is the mass attenuation coefficient, $\mu = \mu_l/\rho$, in cm^2/g
μ_l is the linear attenuation coefficient, in cm^{-1}
ρ is the density of sample, g/cm^3
D is the diameter of the cylinder

For PuO_2, the mass attenuation coefficient[7,8], μ is 6.0609 cm^2/g at 60-keV photon energy and is 3.312 cm^2/g at 129 keV. The density of the WRMs at 20-40 mg Pu loading was ~ 9.81E-5 g/cm^3 and at 2000-4000 mg Pu loading was ~ 9.807E-3 g/cm^3. Here we assumed the bulk matrix and density of diatomaceous earth and the steel containment attenuation effects were consistent for all WRM Pu loadings. For 59.5-keV gamma rays, the calculated CF for the low-loading WRMs was 1.001 and for the high-loading WRMs was 1.104. It accounted for ~10 % of deviation. For 129-keV gamma rays, the self attenuation CF for the low-loading WRMs was 1.0003 and for the high-loading WRMs was 1.056. This difference accounted for ~ 6 %

deviation. There were still a ~ 3 % difference between the normalized count rates of the high- and low-loading WRMs that was not explained by this simple self-attenuation.

The self-attenuation effects of the gamma rays at 375 keV and 414 keV were less than 1 % for all weight ranges of WRMs. Therefore, the Pu verification measurements were based on these two gamma rays. Statistical analyses were performed on three sets of normalized count rates at 375- and 414-keV gamma rays. The F test showed the variances of these three sets of WRMs were equal. Both the t-test and one-way ANOVA (analysis of variance) showed that there was no significant difference between the means of all the WRMs (at 95% confidence level).

Within the limitations of the gamma counting verification, the Pu loadings for each WRM was consistent with the values calculated from the PuO_2 weight for each blend and cylinder loading.

WRM Certification. From the analytical characterizations of the PuO_2 and diatomaceous earth matrix, and the radiometric support measurements on the waste items and the finished WRMs, the CST-8 group of LANL was able to deliver sixty three certified Pu based WRMs to the Phase I NDA PDP Program. A certificate which stated the Pu and Am isotopic information and their measurement uncertainties, the amount of plutonium and alpha activity in each WRM was issued with all the WRMs.

CONCLUSION

Sixty three plutonium based WRMs for the Phase I NDA PDP program were fabricated and certified by the CST-8 Inorganic Elemental Analysis group of LANL in FY 96. All quality

objectives on these WRMs were met to ensure the WRMs contained the NIST or NBL tractability, and accurately and precisely defined quantities of Pu, Am, and total alpha activity.

Radiometric measurements supported many important aspects during the certification of these WRMs. Support included analyses of ^{241}Am, ^{244}Cm, and ^{252}Cf in the PuO_2 sample, determination of PuO_2-DE mixture left in each of WRM waste item, and the final verifications of the uniformity and Pu content of the WRMs.

In FY 97 and FY 98, CST-8 group is preparing several sets of NDA working reference materials for the Phases II and III of the NDA PDP program and other NDA projects. These WRMs will contain increasing amounts of PuO_2, increased particle size of PuO_2, enhanced Am to Pu ratio, and with different nuclear materials (^{238}Pu, ^{241}Am, or enriched uranium isotopes) in diatomaceous earth. The radiometric measurements will continue to support the fabrication and certification of these WRMs.

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