LAUR 97-1160

CONF-970540--1

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April 1997

A manuscript to be submitted for publication in *Applied Radiation and Isotopes* journal.

International Committee for Radionuclide Metrology, 1997
National Institute of Standards and Technology, Gaithersburg, Maryland

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Abstract

Due to the lack of suitable high level National Institute of Standards and Technology (NIST) traceable plutonium solution standards from the NIST or commercial vendors, the CST-8 Radiochemistry team at Los Alamos National Laboratory (LANL) has prepared instrument calibration standards and working standards from a well-characterized plutonium oxide. All the aliquoting steps were performed gravimetrically. When a ^{241}Am standardized solution obtained from a commercial vendor was compared to these calibration solutions, the results agreed to within 0.04% for the total alpha activity. The aliquots of the plutonium standard solutions and dilutions were sealed in glass ampules for long term storage.

Introduction

In any analytical measurement, a good calibration standard is necessary to obtain reliable results. This calibration standard should be traceable to the National Institute of Standards and Technology (NIST) or a certified laboratory or agency (e.g., the New Brunswick Laboratory, NBL). At Los Alamos National Laboratory (LANL), the CST-8 Radiochemistry team performs radiochemical analysis for plutonium and americium at levels of less than 1 nCi per mL to 10 mCi per mL. There are no suitable standardized solutions from the NIST or commercial vendors for these analyses because of the high activity levels and radionuclide type. To meet the requirements for appropriate standard solutions, the Radiochemistry Team prepared standards from a well-characterized plutonium oxide (PuO_2). First the PuO_2 was assayed and analyzed for impurities, then ^{241}Am and the plutonium isotopic content was determined by mass spectrometry.

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Materials and Methods

Radiochemistry calibration standard solutions were prepared from a well-characterized plutonium oxide (PuO_2) sample (Batch ID: PEOR3258-STD1). This batch was originally prepared by the LANL Plutonium Facility specifically for the preparation of working reference materials. The PuO_2 powder was blended, calcined (between 900°C and 960°C), pulverized, and screened to generate a stable (low surface area) material. The Radiochemistry team set aside 3 g of the PuO_2 powder from this batch after the analytical characterizations.

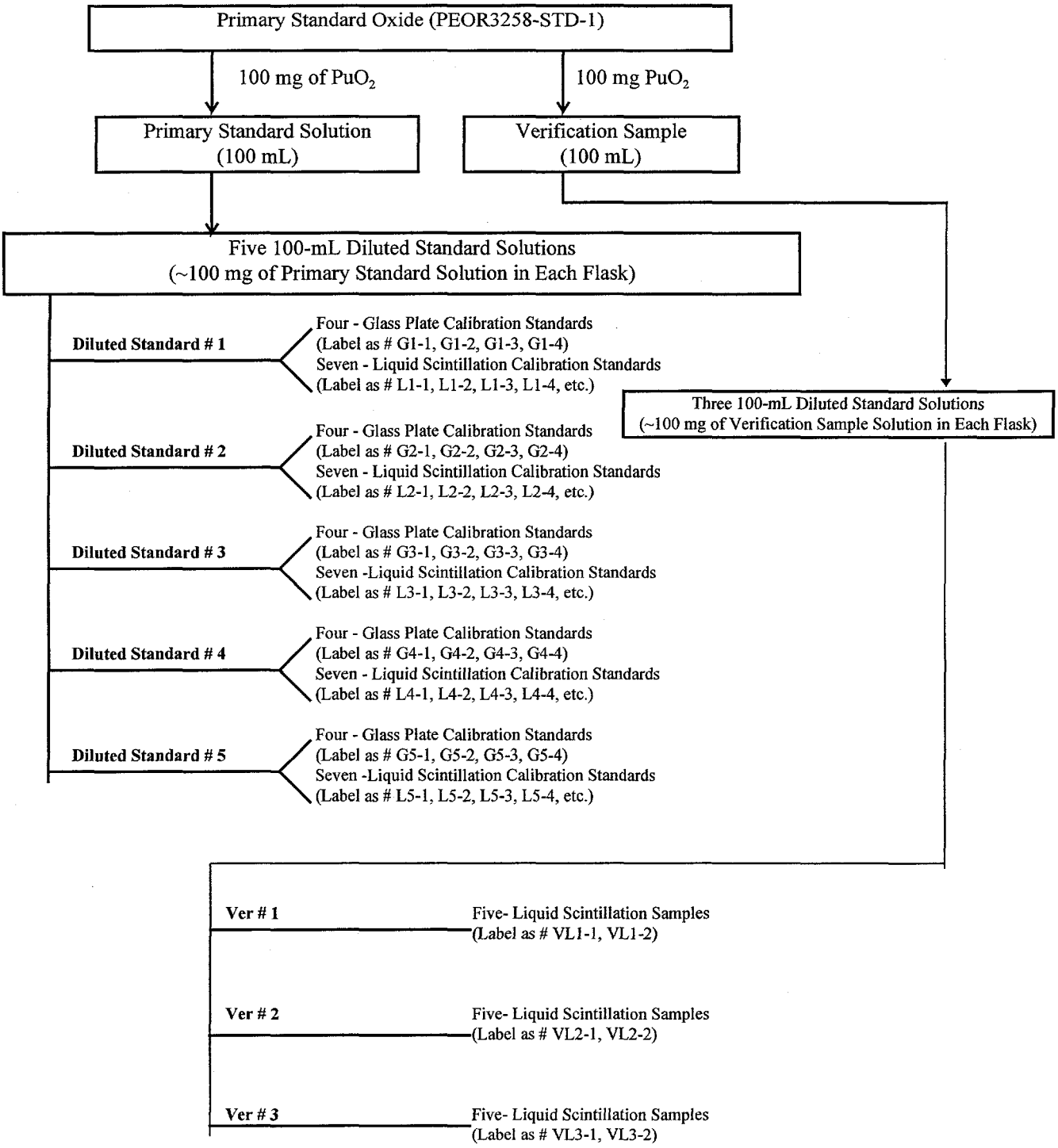
Characterization of Plutonium Oxide. Five samples were taken from the batch of 120 g of PuO_2. The samplings represented different vertical and horizontal regions of the PuO_2 batch in the bottle. Plutonium assay (by coulometric titration), Pu isotopic content (by mass spectrometry), and ^{241}Am analysis (by mass spectrometry and radiochemistry) were done on these five samples of PuO_2. Analyses were done on three aliquots of samples to determine particle size distribution, metallic impurities (by DC Arc Emission and ICP-MS), and anion composition (by ion chromatography) of PuO_2 sample. Alpha spectroscopy was used to determine ^{244}Cm and ^{252}Cf levels in the PuO_2 sample. 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).

Preparation of Primary Standard and Verification Sample. Two 100 mg cuts of PuO_2 were taken from the 3 g oxide sample reserved for the Radiochemistry standard. The aliquots were dissolved by the Pu Assay team which has extensive experience at dissolving PuO_2. Each aliquot was weighed to the nearest 0.01 mg. The dissolution method was ASTM C1168-90 "Standard Practice for Preparation and Dissolution of Plutonium Materials for Analyses." This method employs a sealed reflux tube dissolution using a mixture of HCl, HNO_3, and HF under

pressure to ensure complete dissolution. These solutions were quantitatively transferred to two weight calibrated 100-mL volumetric flasks. One of the flasks was labeled as "Primary PuO_2 Standard," and the other was labeled as "Verification Sample." The solutions were diluted to volume with 4 N HCl. The weight of the solutions was recorded. In these PuO_2 solutions, the expected concentration was 1.001 mg PuO_2/g solution. The alpha specific activity was 68.15 μCi/g solution for the Primary Standard and was 68.13 μCi/g solution for the verification sample.

Preparation of Diluted Standard Solutions. The Primary Standard and Verification Sample solutions were too concentrated for preparation of gross alpha standard. Consequently, dilutions and aliquoting were required. Special disposal plastic pyconometers made from plastic transfer pipettes were used to transfer and weight the plutonium solutions. All the dilution and aliquoting steps were performed gravimetrically. Five aliquots of primary standard dilutions and three aliquots of verification sample dilutions were prepared. Figure I shows the schematic for preparing the primary standard and verification sample. The solution aliquot weights ranged from 93 to 160 mg. The aliquots were diluted in weight calibrated 100-mL volumetric flasks. The dilution and weighing steps were performed quickly to minimize any loss due to evaporation. These diluted plutonium solutions contained approximately 0.9 to 1.5 μg (~60 to 104 nCi) PuO_2 per gram of solution.

Figure I. Schematic on Preparation of Radiochemistry Calibration Standards.



Verification Measurements of Plutonium Oxide Solutions. The diluted primary standard and verification sample solutions were compared by liquid scintillation (LS) counting. The counting efficiency of a LS counter for alpha particles is around 100 ± 1 %. Five LS samples were prepared from each dilution. Approximately 0.1 to 0.5 g diluted solution was added to the plastic LS vial. Then 10 mL biodegradable LS cocktail (Packard Ultima Gold XR) was added to the vials. In addition, two more LS samples were prepared from each of the primary standard dilutions using glass scintillation vials. All LS vials were counted for 10 minutes each on the Packard Tri-Carb 2200CA LS counter. Each vial was counted twice on two separated days.

Preparation of Commercial ^{241}Am Standards. The ^{241}Am standardized solution (AMP10040, batch 95/241/49) was purchased from the Amersham Corp. (Arlington Heights, IL). This standardized solution is directly traceable to the National Physical Laboratory (NPL in the U.K.). A total of 68.25 μCi (as of January 6, 1987) of ^{241}Am activity was transferred quantitatively to a calibrated 50-mL volumetric flask. The standard certificate gave the total uncertainty of ± 0.80 % at 99.7% confidence (3 σ). Five aliquots (90 to 180 nCi) of diluted Amersham ^{241}Am standard solution were prepared for the LS counting. The commercial ^{241}Am LS samples were used to verify the alpha counting efficiency of the LS counter, which was established by the Radiochemistry primary standard and was verified by the verification sample previously.

Standardized Solutions Preservation and Storage. The concentrations of plutonium primary standard and verification sample, plutonium diluted solutions, and ^{241}Am diluted solutions were carefully checked and recorded in the Radiochemistry Laboratory Standard Notebook. Aliquots of these standard solutions were sealed in glass ampules. Each ampule

contained ~ 5 to 12 g of solution. The weight of solution and the amount of radioactivity in each glass ampule were recorded. Then the exterior of each glass ampule was checked for contamination. Each labeled ampule was placed in a heat sealed plastic bag and stored in an upright position in a tray.

Results and Discussion

Characterization of Plutonium Oxide.[1] The results of analytical characterizations of the PuO_2 samples are reported in the Reference 1 and summarized in Table I. Plutonium assay and Pu isotopic distribution and ^{241}Am content are the key components for calculating the alpha specific activity of the radiochemistry standards.

Table I. Plutonium Assay, Isotopic Distribution, ^{241}Am Analysis, ^{244}Cm and ^{252}Cf level

Component (Five aliquots, duplicate analysis performed on each aliquot)	Weight percent at 95% CL[(b)]
^{238}Pu[(a)]	0.000145 ± 0.000008
^{239}Pu	0.937614 ± 0.000013
^{240}Pu	0.059445 ± 0.000005
^{241}Pu	0.002237 ± 0.000008
^{242}Pu	0.000559 ± 0.000004
^{241}Am	766.7 ± 2.2 μg/g PuO_2 by mass spectrometry 762.4 ± 2.6 μg/g PuO_2 by radiochemistry
^{244}Cm	< 0.5 μg/g PuO_2 by alpha spectrometry
^{252}Cf	< 0.1 μg/g PuO_2 by alpha spectrometry
Plutonium Assay (Five aliquots, duplicate analysis performed on each aliquot)	Coulometric titration at 95% CL[(b)]
g Pu / g PuO_2	0.87827 ± 0.00072

(a) ^{238}Pu was determined based on alpha spectrometry and mass spectrometry methods.

(b) The uncertainty of these values was estimated based on long term and short term measurement uncertainty at 95% CL.

Alpha Specific Activity of the Plutonium Sample. The alpha specific activity is calculated using the plutonium assay, the Pu and Am isotopic composition of the PuO_2, the half-life of each isotope, and the % alpha emission for each isotope[2,3]. The calculated alpha specific activity for the radiochemistry standard (PEOR3258-STD1) was 77.1140 mCi/g of plutonium or 67.73 mCi/g of PuO_2 (87.827 % Pu) on July 15, 1995. The uncertainty of PuO_2 specific activity which included the uncertainties of Pu and Am isotopic specific activity and isotopic abundance was ± 0.36 % at 95 % confidence level.

Standards Comparison. The plutonium and americium standards were compared by determining the alpha counting efficiency of a Packard LS counting using each solution. The alpha counting efficiency of the LS counter was determined from the average counts per minute in the alpha region of the LS spectrum. The LS counting efficiency data for primary standard dilutions, diluted verification samples, and ^{241}Am solutions on the Packard LS counter are summarized in Table II. The counting efficiency for alpha particles determined by the primary dilution standards was 100.20 ± 0.12 %. The uncertainty of measurements is expressed as $\pm t * \sigma/\sqrt{n}$. There were no difference in counting efficiency between plastic and glass scintillation vials. The glass vials did give a broader alpha particle peak. From the data set, the third and fourth dilutions (L3-x, L4-x) were clearly affected by possible transcription error during the initial aliquoting step for dilution. However, the overall precision of all measurements was good. The counting efficiency determined by the verification sample dilutions was 100.26 ± 0.05 %. There was an excellent agreement (within 0.06 %) between the counting efficiencies obtained from the primary standard and the verification sample.

The ^{241}Am standard solution purchased from Amersham was used to verify the plutonium measurements. The LS counter alpha counting efficiency obtained by the ^{241}Am activity was 100.18 ± 0.21 %. The difference of counting efficiency obtained from the Radiochemistry plutonium standard and the commercial source was only 0.04 %. The overall counting efficiency of the Packard LS counter was 100.21 ± 0.40 %. The uncertainty of ± 0.40 % included the uncertainty of PuO_2 alpha activity and measurements at 95 % CL. This good agreement between all the results suggests that the Radiochemistry PuO_2 standard solutions are indeed well-characterized and prepared. The solutions prepared from the PuO_2 standard can be used to prepare high quality instrument calibration standards and working standards.

Table II. Liquid Scintillation Data on Radiochemistry PuO_2 Standards and ^{241}Am Solutions

Primary Standard[1]			Verfication Sample[2]			Amersham ^{241}Am[3]	
Counting Efficiency			Counting Efficiency			LS Sample	Counting Eff., %
Dilution	AVG	STD	Dilution	AVG	STD	L1Am-96	100.44
PR-Dil #1	100.13	0.05	VR-Dil #1	100.31	0.08	L2Am-96	100.11
PR-Dil #2	100.08	0.07	VR-Dil #2	100.13	0.15	L3Am-96	100.09
PR-Dil #3	99.54	0.05	VR-Dil #3	100.34	0.05	L4Am-96	100.25
PR-Dil #4	101.07	0.07	Overall AVG = 100.26 ± 0.05 %[4]			L5Am-96	99.99
PR-Dil #5	100.15	0.12				AVG = 100.18 ± 0.21 %[4]	
Overall AVG=100.20 ± 0.12 %[4]							

(1) For each primary dilution, seven LS samples were prepared. Each LS sample was counted twice.
(2) For each verification dilution, five LS samples were prepared. Each LS sample was counted twice.
(3) For ^{241}Am standardized solution, five LS samples were prepared. Each LS sample was counted twice.
(4) The uncertainty of measurements is expressed as $\pm t * \sigma/\sqrt{n}$.

Uncertainty Estimate[4,5,6]. The details of all the measurement uncertainty estimates are given in Reference 5. The uncertainties in the measurement results are estimated based on the random and systematic errors of the measurements, and they are expressed at the 95 % confidence level.

Conclusion

Using a well-characterized PuO_2 sample, standards of high quality for calibrating radiochemistry instrumentation were prepared. The overall uncertainty in the alpha specific activity (μCi/g solution) of primary standard solution and verification sample solution is ± 0.35% at 95 % CL. With accurately known alpha specific activity and through decay corrections, these standardized solutions will be used as the calibration standards for the Radiochemistry team.

Acknowledgment

The authors thank all the members of CST Analytical Chemistry Groups who performed the characterizations of PuO_2 materials. Special thanks to Bob Marshall, the project leader of Working Reference Materials Program, who provided the radiochemistry the PuO_2 materials; and to the Pu Assay team, who provided the dissolution of PuO_2 samples; and to Larry Bruckner and Larry Ticknor, the statisticians of ESA-1, who helped us to determine the uncertainty of the PuO_2 characterizations.

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