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DESIGN OF STANDARDS FOR NONDESTRUCTIVE  
ASSAY OF SPECIAL NUCLEAR MATERIAL

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# Design of Standards for Nondestructive Assay of Special Nuclear Material

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## Abstract

Nondestructive assay (NDA) of special nuclear material (SNM) involves a variety of measurement techniques, instruments, and nuclear materials. High-quality measurements require well-characterized SNM standards that represent the expected range of mass, chemical composition, and physical properties of the SNM to be measured. Due to the very limited commercial availability of NDA standards, facilities must usually produce their own standards, both to meet their specific measurement needs and to comply with existing regulations. This paper will describe the current extent to which NDA standards are commercially available. We will further describe the types of NDA standards used to calibrate and verify the measurement techniques commonly used in the safeguards of SNM. Several types of NDA standards will be discussed in detail to illustrate the considerations that go into specifying and designing traceable, representative standards for materials accounting measurements.

## I. Introduction

The nondestructive assay (NDA) of special nuclear materials (SNM) involves the measurement of the radiation emitted by samples of the material to determine the amount of material present, its isotopic composition, or both. These measurements must be carefully calibrated - or verified in the case of plutonium isotopic measurements. The calibration procedure involves establishing or verifying the response of the measurement instrument to known quantities of nuclear material, by applying the assay technique in question to thoroughly characterized samples that contain well-known quantities of the nuclear material. The samples used in this way will be referred to as working NDA standards.

The outcome of the nuclear material measurement can be affected by many parameters associated with the sample, such as

- the masses of the isotopes of the nuclear materials
- the chemical form and stoichiometry of the material [e.g., oxide(s), fluoride, pure element]
- the physical form of the sample material (e.g., powder, metal, ceramic, liquid)
- the physical attributes of the sample (e.g., shape, fill height, etc.)
- impurities in the sample

The most authoritative guide for calibrating NDA systems (Ref. 1) insists that a calibration standard is "an item physically and chemically similar to the items to be assayed" and "must be chosen so that their contained masses of the nuclide(s) of interest span the mass range expected for the items to be assayed." These conditions, taken to the extreme, would require an inordinately large suite of calibration standards at typical nuclear facilities with a large variety of nuclear materials. Fortunately, the measurement physics underlying NDA techniques is sufficiently well known that many of the parameters that can influence the outcome of the measurement can be identified and corrected for during the measurement and calibration processes, thereby greatly reducing the range of calibration standards required for acceptable calibration of the measurement instruments (Ref. 2). This measurement physics is presented in many sources (e.g., Refs. 3,4) and will not be discussed in detail

here. The objective of this paper is to summarize the basic principles associated with fabrication of calibration standards or reference materials. A more extensive treatise on the preparation of NDA calibration standards will be presented in a forthcoming publication (Ref. 5)

## **II. Brief Discussion of Preparation of NDA Standards from Reference Materials**

Some general preparation procedures are given here which will result in technically defensible reference materials whose reference values are traceable to the national measurement system (see Fig. 1). Most of these procedures follow the recommendation of American Society for Testing and Materials (ASTM) Standard Guide for Preparation of Working Reference Materials (WRM) for Use in the Analysis of Nuclear Fuel Cycle Materials (Ref. 6). In this paper, we will point out the specifics applicable to the preparation of working reference materials for NDA, which are the prepared nuclear material from which sets of NDA calibration standards are fabricated. The activities in each of the preparation steps should be well documented, as part of the facility measurement control program.

### **1. Planning the Standards Fabrication Process**

The preparation of WRM requires planning of procedures before the work starts, in order to ensure the credibility of the completed WRM. The preparation procedure should cover the entire project in detail and should be reviewed to minimize the potential problem areas. It should include at least the following: the intended use of the WRM, the selection and preparation of the special nuclear material, sampling plan and sample characterization, packaging, verification measurement and statistical analysis to establish the reference values and their uncertainties.

### **2. Preparation of the Batch of WRM**

The starting materials for the preparation of the WRM may be material taken directly from a process run and characterized and packaged as WRM. Alternatively, other materials may be processed into the desired forms for WRM. For example, high purity uranium metal might be dissolved, specific amounts of impurities added to the solution, and the solution converted into uranium dioxide after thorough mixing to produce a WRM with specific impurities.

Once the starting material is selected or produced, the material should be homogenized. This can be accomplished by dissolution of the SNM and subsequent precipitation, or by blending a batch of oxides for an extended period of time (several hours). The homogenized starting material is then analyzed, using destructive analysis techniques which themselves are calibrated with appropriate working reference materials. Since the chemical analysis is performed on small samples from the batch of starting material, it is important for the batch to be homogeneous so that selected samples are representative of the entire batch.

The homogeneity of a batch of WRM can be tested approximately by NDA, either by measuring the isotopic distribution looking at a small portion of the batch using a collimated detector, or by neutron counting of small samples. These methods can determine the homogeneity to roughly 1%. More precise tests of homogeneity can be performed by DA or (if the sample is plutonium) by calorimetry. Both of these methods can determine the SNM concentration to a few tenths of one per cent. Usually if the analysis of five to six samples from a batch of WRM agree statistically, the batch can be considered homogeneous.

The form of WRM can be any stable state of the element of interest. Causes of instability include chemical reactions, problems in insuring stoichiometry, and radioactivity. The forms most commonly used for nuclear materials have been oxide powder, pellets or metals. Once the WRM is prepared, it is important that it will not change its characteristics for the estimated shelf life. For hygroscopic materials (such as Pu oxide), high-firing of the oxide to a relatively high temperature (950° to 1000°C) will render the material stable and unlikely to absorb moisture (Ref. 7). The moisture content of every sample should be determined by performing the weight-loss-on-ignition (LOI) test. The standard should also be well sealed to prevent moisture or impurity pickup.

### **3. Preparation of NDA Working Standards by Weighing**

Weighing is by far the most precise measurement, and most of the calculation of the final masses of well-characterized SNM samples is carried out on this basis. The capacity of the scales or balances used should be within the range of the weights to be determined and at least a factor of ten more accurate than required for the

NDA measurements. Before and after use, the balances should be checked with certified weights that are traceable to the national measurements system.

Let us take the case of preparing diluted plutonium oxide standard for gamma-ray assay. Graphite or diatomaceous earth are examples of some of the typical diluents. There are two ways to weigh the SNM:

- The empty inner can is weighed first. Next the plutonium oxide is introduced into the can, and the can plus the oxide are weighed, yielding the net weight of plutonium oxide. This case requires the plutonium concentration of the pure oxide to be determined by DA. The diluent is added after the weighing, and the blending is done after the inner can is sealed.
- The already-diluted plutonium oxide is introduced into the inner can. This case requires the plutonium concentration of the diluted oxide to be determined by DA, which requires the dilution to be thoroughly homogeneous. This is potentially a much harder determination, especially if the diluent cannot be readily dissolved. (Both graphite and diatomaceous earth are difficult to dissolve.)

#### **4. Container and Packaging**

It is important that the container material is compatible chemically with the WRM matrix (diluent) and does not contribute significantly to the assay signal. For example, plastic bottles should not be used to contain neutron standards, because plastics tend to moderate the neutron spectrum and thereby alter the response of the measurement system. Some plastics also contains fluorine which will increase the (alpha, n) signal of the standard.

Usually, aluminum, steel, and stainless steel containers are used to package the WRM. Steel (food) cans can be secured by a rolled seal, such as that encountered in the food packing process. However, food pack cans are usually relatively thin and tend to deform with usage. A better choice is aluminum or stainless steel, which would require welding to seal the container. Regardless of the container material, the attenuation of the gamma rays due to the container should be taken into account in the calibration of the instrument. After the container is packaged, it should also be leak tested.

#### **5. Sampling and Characterization of the WRM Batch**

Of all the steps of preparation of standards, sampling and characterization are probably the most important and need to be planned carefully. These processes determine the uniformity of the batch of WRM and the amount of nuclear material in each standard. Characterization by calibrated analytical techniques provides traceability to the national system of measurements.

Sampling is relatively simple if the WRM is uranium, plutonium or mixed oxide (MOX). The oxide batch is mixed and blended, and samples are taken from different parts of the batch in order to test homogeneity. A slightly different procedure is recommended if the WRM is fuel pellets. After several fuel pellets are selected from the batch, a few are dissolved and analyzed destructively to verify pellet-to-pellet homogeneity. If homogeneity is established, then the remaining pellets are used as standards. Homogeneity can be assessed by measurement of the oxide-to-heavy-metal or the U/Pu ratio in the pellets. This same approach can also be applied to fuel rods. At least one of the samples should be analyzed for impurities, to limit the influence of the presence of these impurities. Some archive samples should also be kept in case of questions concerning the standard.

The traceability of analytical measurements begins with certified reference material (CRM). These materials are usually in the form of pure metals, small quantities of which are dissolved, as needed, to form working standards for the destructive analysis measurements. CRMs are available from laboratories that are certified by the national measurement system to produce these highly-pure materials. To supplement elemental CRMs, isotopic CRMs are also available, to support calibration of mass- and alpha-spectrometry analyses.

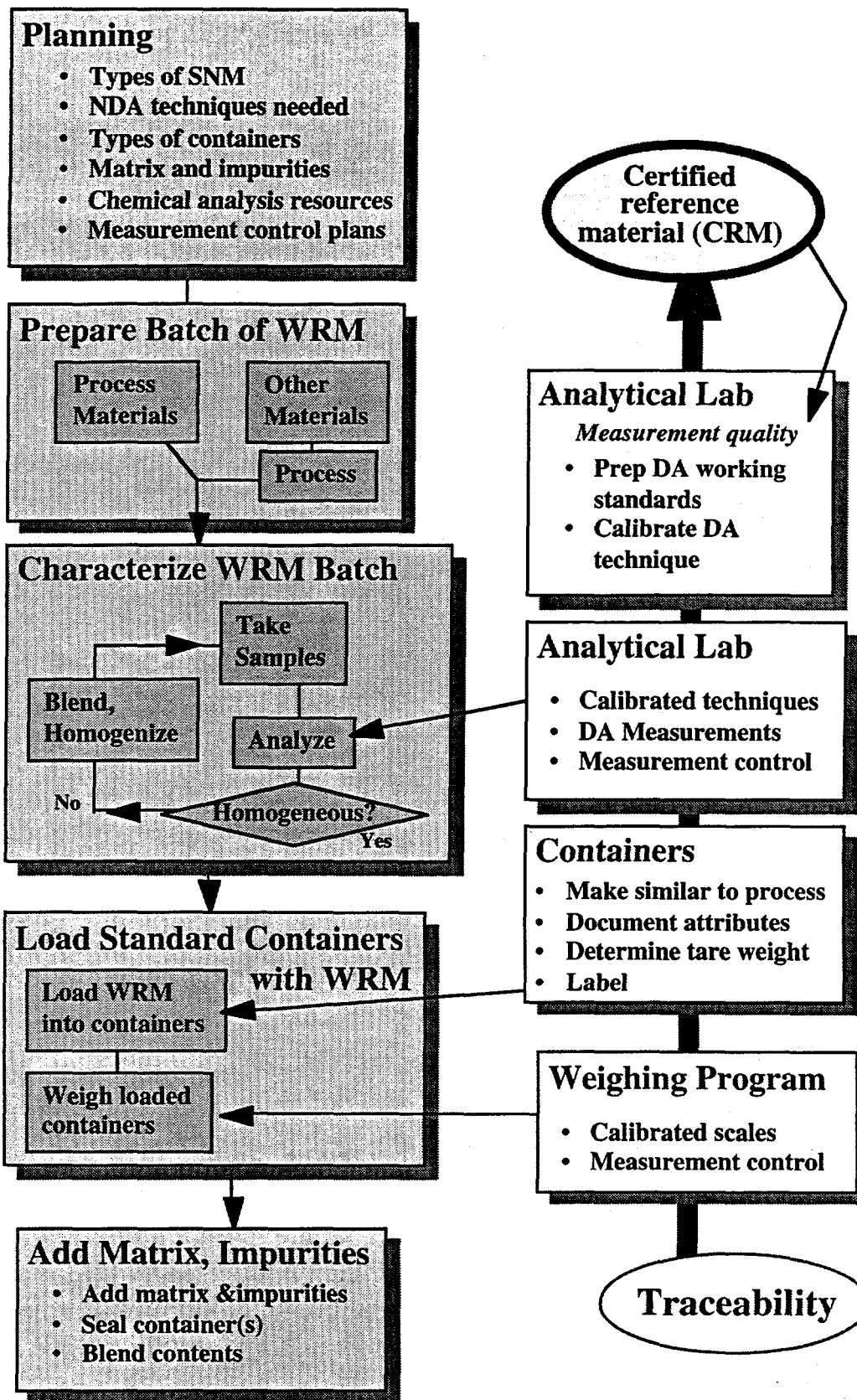


Figure 1. Schematic of the Process of Preparation of NDA Working Standards. The standards preparation process is depicted on the left, and the elements of the traceability of the standards to the national measurement system are indicated on the right.

Because the types and quantities of CRMs for NDA is fairly limited, they cannot be used directly to make up batches of WRM. However, CRMs are used to generate working DA standards, to calibrate the analytical methods used for establishing the concentration values (reference values) assigned to the WRM. This provides traceability of all analytical and NDA measurements back to the national measurement system. Uranium and plutonium concentration CRMs are available from NBL as well as IRMM in Europe. Uranium and plutonium isotopic CRMs are also available from NBL and IRMM (Ref. 8)\*.

The analysis method selected to characterize the batch of WRM should be appropriate for the samples to be analyzed. For example, mass spectrometry should be used to determine  $^{239}, ^{240}, ^{241}, ^{242}\text{Pu}$  isotopic distribution, and alpha spectrometry should be used to determine the  $^{238}\text{Pu}$  and  $^{241}\text{Am}$  isotopic distribution. The uranium concentration of a sample can be determined by means of the Davies-Gray technique, and plutonium concentration can be determined by means of controlled-potential coulometry. Because of the importance of DA and its traceability to the national measurement system, it is desirable, whenever possible, to have two independent laboratories perform the analyses. This will minimize the chance that standards are produced with undetected bias.

There is also a question of how accurate the destructive analyses should be. A general guideline is that the DA should be a factor of 3 to 5 more precise and have 1/3 to 1/5 of the bias anticipated in the measurement of the unknowns. For example, in preparing neutron standards where the measurement precision is typically 1%, the analysis to characterize the WRM should be performed with a precision of ~0.2%. The contribution of the DA uncertainty to the overall error of the NDA would then be relatively small, 0.04% in this case. In the case of standards for waste measurements by segmented gamma scanning (SGS), the assay precision and bias are typically around 5%. DA precision of 1 to 2 % is therefore acceptable, and it is quite possible that the less expensive approaches of calorimetry and isotopic combinations are sufficient to quantify waste WRM.

#### **6. Verification**

Once a set of NDA standards is produced that covers a range of SNM masses, verification measurements should be performed to check the consistency of the set of WRM. This is particularly important for WRM in solution form. NDA assay systems for solutions can achieve 0.1 to 0.2% precision and bias. The total corrected counts/gm of SNM should be consistent for all WRMs. An example of the verification measurement of a set of SGS can standard is given in Reference 9.

### **III. Examples of NDA Calibration Standards**

#### **A. Uranium Enrichment Measurements**

Determination of uranium enrichment is a key measurement in uranium enrichment and fuel fabrication facilities and for international safeguards.

##### **1. Measurement Principles**

$^{235}\text{U}$  decays by alpha emission to excited levels of  $^{231}\text{Th}$ , which in turn emit gamma rays of various energies, the most prominent of which has an energy of 185.7 keV. If the uranium sample is large enough, then the gamma rays originating from deep within the sample are completely absorbed and do not contribute to the gamma-ray intensity observed at the surface of the sample. Thus, with increasing sample thickness the 186-keV gamma-ray intensity at the surface reaches an equilibrium value, which is almost independent of the physical form of the sample. For pure uranium compounds this value is proportional to the  $^{235}\text{U}$  enrichment of the sample, and generally only small corrections for chemical composition have to be applied. This is the "enrichment meter" principle, and its application requires that the sample under assay is thick enough to be opaque for 186-keV

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\* The Central Bureau of Nuclear Measurements (CBNM) in Geel, Belgium has changed its name to the Institute of Reference Materials and Measurements (IRMM). The US National Bureau of Standards (NBS) has changed its name to the National Institute of Science and Technology (NIST). The agent that sells the CRM standards for the NIST is the New Brunswick Laboratory (NBL) at Argonne, Illinois.



gamma radiation (see Ref. 3, Ch. 7). All measurement parameters that affect the observed counting rate must be carefully controlled and corrected for and are shown schematically in Figure 2.

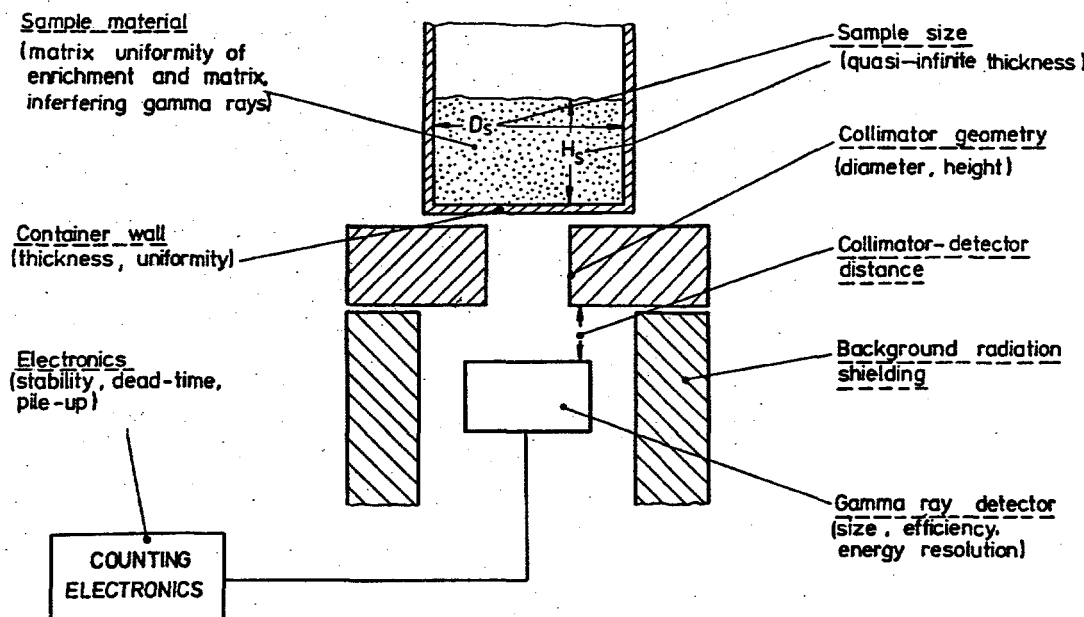


Figure 2. Parameters affecting the accuracy of gamma-ray-spectroscopic  $^{235}\text{U}$  enrichment measurements based on the "enrichment meter" principle.

The relation between the  $^{235}\text{U}$  enrichment,  $E_5$  (expressed in %), and the net peak counting rate,  $N_{186}$ , of 186-keV photons detected is influenced by many factors, as shown in Eq. 1:

$$E_5 = 100 \cdot N_{186} \cdot \frac{4\sigma \cdot T_{1/2}}{P_{186} \cdot \ln 2} \cdot \frac{1}{F \cdot V \cdot \epsilon} \cdot C_m \cdot C_w \cdot (C_1 + C_I) \quad (\text{Eq. 1})$$

where

- $N_{186}$  = observed net peak counting rate of 186-keV photons
- $\sigma$  = photon attenuation cross section at 186 keV for uranium
- $T_{1/2}$  = half-life of  $^{235}\text{U}$
- $P_{186}$  = branching ratio of 186 keV photons
- $F$  = collimator cross section
- $V$  = solid angle formed by collimator and detector
- $\epsilon$  = intrinsic detector efficiency
- $C_m$  = correction for gamma attenuation in sample matrix materials
- $C_w$  = correction for gamma attenuation in sample container wall
- $C_1$  = correction for counting rate losses caused by counting electronics
- $C_I$  = correction for interference due to photons from isotopes other than  $^{235}\text{U}$

A detailed discussion of this equation can be found in Reference 10.

## 2. Physical criteria for enrichment standards

An enrichment standard has the following requirements:

- a. The sample must be "quasi-infinitely" thick for 186-keV gamma rays, as described above. This condition inherently restricts the method to relatively thick samples. A discussion of this is given Reference 5.
- b. The sample must be isotopically uniform. When mixtures of differently enriched materials are assayed, the sample material must be carefully homogenized prior to the measurement.

- c. The container wall thickness must be reasonably thin so that the correction for attenuation in the wall is relatively small. If the container wall is thick, then the gamma attenuation correction must be experimentally determined.

Enrichment measurements using the "enrichment meter" principle will give accurate results only if the sample is sufficiently thick to be opaque for 186-keV gamma rays. For 7-cm diameter samples, the approximate minimum values of the sample mass for  $\text{UO}_2$  and  $\text{U}_3\text{O}_8$  powders are:  $M = 202.5$  g for  $\text{UO}_2$  powder, and  $M = 209.7$  g for  $\text{U}_3\text{O}_8$  powder. The Certified Reference Material (CRM) EC-NRM-171/NBL-SRM-969 is based on this calculation with 200 g of  $\text{U}_3\text{O}_8$  in each standard, with a sample height of 2 cm. This is to minimize the amount of SNM required.

### 3. Preparation and examples of enrichment standards

Two sets of enrichment standards should be mentioned: one is the EC-NRM-171/NBS-SRM-969 which was jointly certified by the Central Bureau of Nuclear Measurements in Geel, Belgium (CBNM) and by the US National Bureau of Standards (NBS). This well-documented set has enrichments from 0.3% to 4.5%, which is adequate only for the low enrichment fuel cycle (Ref. 10). We have been told that IRMM and NBL are preparing additional standards with higher enrichments.

The second set is a suite of Working Reference Materials (WRM) at Los Alamos National Laboratory (LANL). This set has 19 1-kg cans of uranium oxide (that were acquired over a period of many years) with 12 enrichments between natural and 91 atom %. They were packaged in different containers and had only routine determinations of isotopic ratios and uranium fraction based on a single sample. In 1985, the Los Alamos repackaged and re-characterized these 19 uranium oxide samples (Ref. 11). Of the 19 WRMs, seven were found to be homogeneous and could be declared as primary enrichment standards.

From each of the 19-kg lots of uranium oxide, six 2-gm samples were collected from different parts of the oxide. Of the six samples, three were analyzed by LANL, two were submitted to the Department of Energy's New Brunswick Laboratory (NBL) for similar analyses, and one sample was put into archival storage for possible future analyses. The most important analysis is, of course, the isotopic distribution; the uranium fraction is of secondary importance. The isotopic distributions and other important parameters of the 7 primary standards are shown in Table 1.

Table 1. Parameters of primary enrichment standards at LANL

Standard ID	$^{235}\text{U}$ (at.%)	Std. Dev. +/-	U mass (g)	Approx. Oxide Depth (cm)	Approx. Oxide Density(g/cm <sup>3</sup> )
UIISO-91	91.419	0.011	990	7.7	1.7
UIISO-66	66.317	0.032	990	5.6	2.3
UIISO-52	52.426	0.004	989	5.8	2.2
UIISO-38	37.848	0.015	991	6.0	2.1
UIISO-13	13.098	0.008	991	5.4	2.4
A1-324-1	10.202	0.003	987	4.6	2.8
A1-324-2	10.200	0.001	987	4.1	3.1

These 7 uranium oxide standards span the range from 91% to 10% and complement very well the CRM EC-NRM-171/NBS-SRM-969 set. To perform enrichment measurements over a wide enrichment range, both sets of standards should be used.

### B. Plutonium isotopic standards

Information about the isotopic composition of plutonium is important for the verification of the total mass of Pu by neutron coincidence counting or by calorimetry. Accurate and precise information about the abundances of Pu and  $^{241}\text{Am}$  is needed because neutron-coincidence counting (NCC) measurements represent only the even-mass Pu isotopes. The isotopic abundances are also necessary for the calculation of the correction for the ( $\alpha$ ,n) reactions as part of the neutron multiplicity correction. Also, since each Pu isotope and  $^{241}\text{Am}$  has a different specific power, the Pu isotopic abundances are also needed to interpret calorimetry measurements. Although mass spectrometry has historically been used to measure isotopic abundances, methods using gamma-ray spectrometry

have been developed for use in nuclear safeguards measurements. Gamma-ray spectrometry offers advantages over mass spectrometry, because the measurements are nondestructive, less time consuming, and less expensive.

An important element in the application of gamma-ray spectrometry are plutonium isotopic standards to calibrate and verify performance of a measurement system, to test and compare the measurement and data-analysis methods being used, to investigate the sources of errors, and when possible to improve the knowledge about gamma-ray emission probabilities.

### 1. Measurement Principles

The basis for the measurement of the amount of any radioactive isotope by gamma-ray spectrometry is given by

$$I = E \cdot P \cdot X \quad (\text{Eq. 2})$$

where

$I$  = the measured intensity of a peak corresponding to a gamma ray of a specific energy  
 $E$  = the overall detection efficiency or counting efficiency  
 $P$  = the emission probability per decay of the gamma ray being measured, and  
 $X$  = the amount of the radioactive isotope present in the sample.

$P$  is a fundamental constant, related only to the nuclear decay properties of the isotope being measured. However, its value may be uncertain, because it is experimentally measured. The value of  $E$  depends on a number of factors, some of which are quite complex or cannot be easily defined or determined.

In choosing a gamma-ray spectrometry method, it is useful to divide sample measurements into two categories: those in which the counting geometry and thus the counting efficiency can be controlled (reproducible or calculable) and those where this control is not possible. An example of the first category is the assay of uniform solution samples whose volume and counting position can be controlled easily. For this type of measurement, it is usually easier to combine the terms  $E$  and  $P$  in the above equation into a single calibration constant for each gamma ray peak that is being analyzed. One or more appropriate standards are used to calibrate the spectrometer system. The calibration constants that are generated can be used in the analysis program to interpret spectra obtained from unknown samples.

Many samples, however, particularly solid samples, are nondescript, with geometry or matrix composition that are frequently unknown or uncontrolled. For such samples, the method described above usually will not work because the counting geometry or counting efficiency is not reproducible, or because the attenuation of the gamma rays by the sample matrix or other absorbing materials is unknown. A way to minimize the effects of these measurement problems is to take advantage of the similar counting efficiency with which gamma rays of neighboring energies are detected. That is, when the energies are nearly equal, the efficiency and attenuation differences are small, and the ratio of the isotopic abundances can then be directly related to the peak intensities by

$$A/B = I_A/I_B \cdot E_B/E_A \cdot P_B/P_A \cdot t_A/t_B, \quad (\text{Eq. 3})$$

where

$A/B$  = atom ratio of isotopes A and B,  
 $I_A, I_B$  = peak intensities of gamma rays from isotopes A and B, respectively,  
 $E_A, E_B$  = counting efficiencies for the respective gamma rays,  
 $P_A, P_B$  = gamma-ray branching probabilities, and  
 $t_A/t_B$  = decay half lives of isotopes A and B.

The basic method for determining the relative abundances of plutonium isotopes is to measure the intensity of two or more peaks from gamma rays of similar energy, but arising from different isotopes, as shown in the above equation. Because the gamma-ray-emission probabilities and half lives are known, the atom ratios can be calculated, if relative detection efficiencies ( $E_A/E_B$ ) for the peaks can be estimated. A common approach is to use a group of gamma-ray peaks in the spectrum belonging to one or more Pu isotopes to delineate an intrinsic relative-efficiency curve. This curve is determined by fitting observed peak intensities from one isotope's emission spectrum (divided by their gamma emission probability) to a function used to describe the relative efficiency versus

energy (Refs. 12,13). This approach has reduced the demands for truly representative, plant specific reference materials for these measurements. In the remainder of this discussion, we will discuss plutonium standards from the perspective of the gamma-ray measurement methods that use the "intrinsic" efficiency approach to determine relative plutonium isotopic abundances.

## 2. Design Considerations

A plutonium isotopic standard has the following requirements:

1. The plutonium isotopes and  $^{241}\text{Am}$  must be homogeneously distributed in the sample matrix.
2. The isotopic abundances of the plutonium and  $^{241}\text{Am}$  must be well characterized and traceable to the international system. A range of isotopics in the standards representative of the range in samples to be measured is important to identify any possible biases in the analysis. The date of the declaration of the isotopic abundances in a plutonium standard must be known accurately.
3. The container wall thickness should be thin enough so that gamma-ray energies as low as 60 keV are able to penetrate. External absorbers can be used to simulate samples with thicker container walls.

Gamma-ray isotopic analyses that use the "intrinsic" efficiency method should be able to accommodate samples of varying size, geometry, chemical composition, and container wall thickness. However, standards that control the variations in the sample container material and geometry, isotopic abundances, and plutonium mass offer the analysis evaluators the ability to study the effects of these parameters in a systematic fashion.

## 3. Examples of standards

Two sets of plutonium isotopic standards should be discussed. One set is the CBNM Nuclear Reference Material 271 (Pu Isotopic Standards for Gamma Spectroscopy) which consists of four sealed cans, each containing 6.6 grams of  $\text{PuO}_2$  with abundances of 61, 70, 84, and 93 atom %  $^{239}\text{Pu}$ . The can is made of stainless steel and has a maximum outer diameter of 40 mm and height of 21 mm. Complete specifications and details on the analysis of these standards are given in Reference 14. The plutonium isotopic and  $^{241}\text{Am}$  abundances have been well characterized and are given for a specified date. In addition, four other parameters are specified: mass and geometry of the  $\text{PuO}_2$  layer, can window thickness, and the chemical purity of the  $\text{PuO}_2$ . We have been told by IRMM that they have only four sets of this certified reference material still available.

The second set of plutonium isotopic standards (seven sealed Pu oxide samples of different isotopic composition, each containing 0.45 grams) was prepared for the Plutonium Isotopic Determination Inter-comparison Exercise and are commonly referred to as the PIDIE standards. The isotopic composition of each is given in Table 2. Sets were sent to nine participating laboratories for three separate determinations of the unknown isotopic composition. Later, separate small samples were taken from the same batches and analyzed by mass-spectrometry to have reference values for the evaluation of the nondestructive measurement results.

Table 2. Atom % plutonium and  $^{241}\text{Am}$  abundances in the PIDIE samples as of January 1, 1988.

Sample	% Pu-238	% Pu-239	% Pu-240	% Pu-241	% Am-241
1	.0111	93.8212	5.9699	.1978	.2295
2	.0226	89.4634	10.0712	.4428	.2636
3	.0474	84.8340	14.1285	.9901	.6264
4	.1094	78.2371	19.8165	1.8368	1.5750
5	.1332	76.5022	21.3015	2.0634	1.7498
6	.9691	68.8903	24.7031	5.4378	3.7338
7	1.3203	65.1331	26.7815	6.7651	3.6418

The goal of the inter-comparison exercise was to test the gamma-spectrometry methods for measuring Pu isotopic ratios in a large range of isotopic composition, to investigate error sources, and if possible to improve the knowledge of the gamma-ray emission probabilities. The PIDIE samples can be considered as well-characterized samples for the Pu isotopic composition. A complete report on the PIDIE exercise is given in Reference 15.

## **C. Passive Gamma-Ray Assay of Nuclear Material**

### **1. Measurement Principles**

Passive gamma-ray assay of nuclear material involves the measurement of the intensities of specific gamma rays emitted by SNM samples and relating that intensity to the amount of SNM in the sample. These measurements are usually accompanied by significant corrections to the measured intensities for the absorption of the radiation by the container, the SNM itself, and other materials between the SNM and the detector (see Ref. 3, Chs. 1-10). The assay technique that employs these absorption-corrections is called "transmission-corrected gamma-ray assay." Gamma-ray measurements are used to assay solutions and solid samples in essentially all possible chemical forms. Samples can be highly pure product material, low- or high-density contaminated waste, process solutions, or even material held up in process equipment. Selection of calibration standards involves consideration of the expected measurement geometry, the design of the measurement instrument, and the attributes (physical and chemical) of the expected samples to be measured.

In view of the strong interaction of gamma radiation with matter, samples that are large in size or of high density are difficult to measure accurately, because of the uncertainty introduced by the large absorption corrections. Thus, the samples (and therefore the calibration standards) must be of medium to low density and size. A convenient guideline is that if more than 99% of the assay radiation is absorbed by the full thickness of the sample, it is inappropriate to assay that sample by a gamma-ray technique. In many such cases, an assay technique employing measurement of the more penetrating neutron radiation will yield a more reliable assay result.

### **2. Physical criteria for the standards**

The NDA working standards for gamma assay must have the following properties:

- The sample must be of medium thickness and density, so that the gamma radiation measured in the assay is attenuated by no more than 99% by the full thickness of the standards.
- The sample must be uniform with respect to SNM contents. When mixtures of different materials are assayed, the sample material must be carefully homogenized prior to the measurement.
- The container wall thickness must be thoroughly specified, to assure accurate correction for absorption by the container materials.

### **3. Preparation of Standards**

The transmission-corrected assay technique can be applied by either measuring the entire sample in one measurement or by applying the technique independently to segments of a sample and combining the segmented results into an assay of the whole item. Calibration standards for the latter application, known as segmented gamma scanning (SGS), will be discussed here.

#### **a. Pu Oxide Can Standards**

In 1990, four sets of 5 containers of plutonium oxide WRM were produced at Los Alamos for SGS assay of medium-sized samples (Ref. 9). The plutonium oxide was high-fired, blended for more than four hours, and sieved. Six relatively small samples were selected from different parts of the blended batch and sent to three independent laboratories (NBL, Mound, LANL) where the characterization of these samples was performed. The results were compared to verify the uniformity of the batch as well as to determine the g Pu/ g sample. Low burnup plutonium (96%  $^{239}\text{Pu}$ ) was used so that the  $^{241}\text{Pu}$  component was quite low (<0.1% on 1/1/90). Low burnup Pu was selected so that the in-growth of  $^{241}\text{Am}$  would be slow, meaning that these standards could be used for a long time before the radiation level would exceed the threshold for precaution in handling.

These standards were contained in tall, narrow-diameter, stainless steel cans designed specifically for segmented gamma scanning. The matrix material used was diatomaceous earth with a density of 0.26. For each of the cans, a weighed amount of the high-fired plutonium oxide was introduced into the inner can, diatomaceous earth was added, and the lid was then welded shut in a glove box. The inner can was then bagged, placed in the outer can which was again welded, outside of the glove box. Then each can was blended, and a vertical gamma scan of each can was performed to determine the uniformity of the blended plutonium mixture. If the can did not pass a rigorous uniformity test, blending was repeated.

Table 3. Example set of Pu can standards from the 19 cans prepared in Ref. 9.

Standard ID	$^{239}\text{Pu}$ (g)	Uncertainty (g)	(%)
STDSGB10	9.624	0.012	0.125
STDSGB30	28.890	0.023	0.078
STDSGB100	96.273	0.068	0.071
STDSGB200	192.528	0.135	0.070

b. SGS U drum standard

To calibrate the LANL SGS drum counter, a set of uranium drum standards was prepared in 1991-1992 (Ref. 16). It was prepared in the same manner as the SGS can standards except that it was prepared in a modular manner with 4-liter bottles.

The WRM for the standards was prepared from relatively pure uranium oxide ( $\text{U}_3\text{O}_8$ ) diluted with diatomaceous earth. The feed oxide was high-fired for several hours, sieved through a 100-mesh sieve to produce a particle size less than 150 microns, and blended. Five samples taken from different parts of the blended batch were submitted for chemical characterization. The chemical analysis determined the uranium isotopic composition, the uranium weight fraction, and the loss on ignition. Each bottle, filled with the mixture of uranium oxide and diatomaceous earth, was blended for 60 min and measured with the SGS to test its uniformity. This was performed by measuring the total corrected counts in each segment, from the top of each bottle to the bottom, using the 186-keV gamma peak from  $^{235}\text{U}$  and correcting for its self-absorption in each segment. From the vertical scans, eight of the standards were found to be not sufficiently mixed; they were rebled and rescanned.

Normal 200-l drums are too short to accommodate 4-l bottles stacked three high. Therefore each drum was lengthened by welding two drums together. The filler material in the drum standard was Cellutex; it was used because it has approximately the same density as diatomaceous earth. The Cellutex was precut with seven holes and stacked in the drum and then twenty 4-l bottles of uranium oxide were positioned in each drum. Three drums were prepared according to the specifications in Figs. 7a and 7b. The certified mass of the three drums are listed in Table 4.

Table 4. Mass and uncertainty of the uranium drum standards.

Standard	$^{235}\text{U}$ (g)	Uncertainty $^{235}\text{U}$ (g)
STDSGUD1	31.20	0.07
STDSGUD2	100.99	0.21
STDSGUD3	200.43	0.42

There is one aspect of this set of drum WRM which is less than desirable. With this design, the WRM tends to exacerbate the 'end effect', a phenomenon in which the beginning and ending segments of the assay do not fill the detector field of view with SNM, thereby giving a low result for those end segments. If this effect is not corrected for in the instrument software it will produce a negative bias on the assay of the full drum.

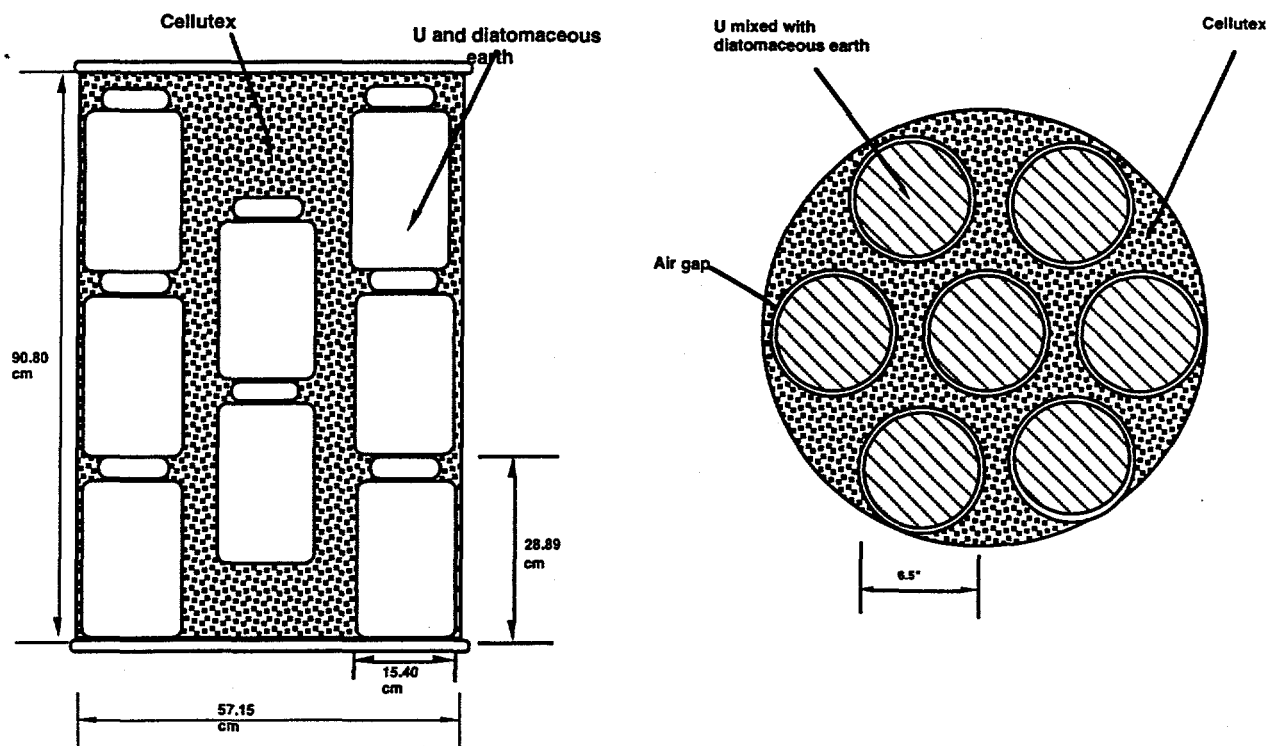


Figure 7a. Side view of the 4-l bottles in the drum in a Cellutex matrix. Figure 7b. Top view of the 4-l bottles in the drum.

## D. Assay of Nuclear Materials by Neutron Coincidence Counting

### 1. Measurement Principles

When SNM isotopes fission (either spontaneously or by being induced), the fission process produces prompt neutron radiation with average multiplicities between 2 and 4, depending on the fissioning isotopes. If neutron assay instrumentation is designed to recognize multiple (correlated) neutron detection events, the observed neutron coincidence count rate will be related to the amount of fissioning material in the sample. The response of the measurement system is sensitive to several effects in addition to the amount of fissioning material:

- Moderating materials in the sample and in the detector will reduce the average neutron energies and will usually increase the response of the system [examples of moderating materials are plastics (especially  $\text{CH}_2$ ) and moisture (water)].
- Alpha emissions by the even-mass SNM isotopes in the sample can interact with matrix materials and produce neutrons [so-called “(alpha,n) interactions”].
- Neutrons in the sample material can induce further fissions, adding to the response of the system as the amount of SNM increases [so-called “multiplication effect”].

Since all of the above effects are usually present in neutron assays, the calibration curves are seldom linear and must be defined with several standards.

Neutron coincidence assays of plutonium samples is possible using the passive neutron signal from spontaneous fissions of the even-mass isotopes. For uranium samples, the passive fission rates are vanishingly small, and so neutron coincidence assays must be performed by inducing fissions in the sample. This is done with random (i.e., uncorrelated) neutrons from an external neutron source, usually  $\text{AmLi}$ . The active neutron coincidence assays therefore measure the sample's fissile (odd-mass) isotopes.

### 2. Design of Standards for the Active-Well Coincidence Counter (AWCC)

A set of enriched uranium oxide standards was fabricated in 1991-1992 (Ref. 17) with the purpose of being used with the Active Well Coincidence Counter (AWCC). The AWCC has two modes of operation: fast and

thermal. In the fast mode, the sample cavity has a cadmium liner that absorbs thermal neutrons; this mode is intended for the assay of large uranium samples. In the thermal mode, the cadmium liner is removed to allow fissions induced by thermal neutrons; this mode raises the sensitivity of the instrument and is intended for measurement of low-mass uranium samples (see Ref. 3. Ch. 17). It was decided that the range of anticipated sample sizes could be covered by 15 standards, grouped into a low-mass set (the  $^{235}\text{U}$  mass range up to 250 g) and a high-mass set (covering the range of 250 g up to 4 kg). Samples below 250 g are to be assayed in the thermal mode, and those above 250 g are to be assayed in the fast mode.

Approximately 18 kg of  $\text{U}_3\text{O}_8$  from four batches were blended into four new bottles by taking approximately the same amount from each batch. These four new bottles were mixed in a blender for one hour. Samples were drawn from each bottle for chemical characterization. The characterization included uranium mass fraction, uranium isotopic distribution, weight loss-on-ignition, and impurity determination.

The standards were packaged into food pack cans; two sizes of containers were used to accommodate all the different masses of  $\text{U}_3\text{O}_8$ . The dimensions of the smaller cans (A) were 12.75 cm dia. x 10.16 cm ht. The dimensions of the larger cans (B), which utilized double containment for the higher-mass standards, were 11.43 cm dia. x 19.05 cm ht. for the inner can, and 12.75 cm dia. x 20.32 cm ht. for the outer can. The masses and the container types for this set of WRM are shown in Table 5.

Table 5. Certified  $^{235}\text{U}$  mass, container and estimated fill height of this set of WRM.

Standard ID	$^{235}\text{U}$ (g)	Uncertainty ( $^{235}\text{Ug}$ )	Container	Est. Fill Height (cm)
STDUO10	9.98	0.02	A	0.1
STDUO25	25.00	0.04	A	0.14
STDUO50	49.95	0.08	A	0.27
STDUO75	75.00	0.12	A	0.79
STDUO100	99.99	0.16	A	1.27
STDUO125	125.00	0.20	A	1.43
STDUO150	149.99	0.23	A	1.69
STDUO250	250.00	0.39	A	2.54
STDUO500	500.00	0.78	A	2.90
STDUO750	750.0	1.2	A	5.08
STDUO1000	1000.0	1.6	A	5.87
STDUO1500	1500.3	2.3	B	7.62
STDUO2000	2000.3	3.1	B	10.2
STDUO2800	2800.2	4.4	B	14.0
STDUO3600	3600.5	5.6	B	18.4

One aspect of this set of AWCC WRM is less than desirable. For some of the low mass standards, the fill height is less than 0.5 cm. Because the AWCC is sensitive to the position of the AmLi activation source relative to the sample, any changes in the distribution of the sample in the can could affect the assay result. In retrospect, for the low mass standards (mass < 50 g), a smaller can with the uranium oxide fixed inside the can would be more desirable.





*Figure 3. Assembly of many of the NDA calibration standards discussed in this paper. In the carrying case are the Geel enrichment standards (NBL-SRM-969). To the left of the carrying case, in the foreground, are the PIDIE Pu isotopic standards; in the left background are the CBNM Pu isotopic standards. To the right of the carrying case are two of the SGS can standards containing plutonium oxide.*

#### IV. Conclusion

At each nuclear facility where materials accounting measurements are performed, the measurement specialists should develop working NDA standards for the measurement techniques in use at the facility. The facility measurement control program begins with the fabrication of well-characterized, traceable standards, followed by a conscientious program to assure that the standards and the measurement techniques retain their high quality. Maintenance of reliable measurement instruments requires

- calibration and use of well-characterized working NDA standards
- careful documentation of the traceability of those working standards to the national system of measurements, and
- a vigilant measurement control program that regularly verifies the validity of instrument measurements, diagnoses the status of the operations of the instrument and of the operators, and documents all findings.

These are the primary elements of a facility-wide measurement control program.

Facilities should also participate in exchange programs whereby results of measurements by their instrumentation are compared with results from other facilities on the same samples. This inter-comparison is especially important among facilities that exchange nuclear material shipments during the course of their operations.

Finally, the facilities will be required by their national MC&A system to verify the continued quality of their measurement results and to report their findings, on a regular basis, to the certifying authority and the national safeguards system.

## V. References

1. "American National Standard Guide to Calibrating Nondestructive Assay Systems," ANSI N15.20-1975 (American National Standards Institute, New York, 1975).
2. J. L. Parker, "The Use of Calibration Standards and the Correction for Sample Self-Attenuation in Gamma-Ray Nondestructive Assay," Los Alamos National Laboratory Report LA-10045 (1984, revised 1986).
3. T.D. Reilly, N. Ensslin, and H.A. Smith, Jr., and S. Kreiner, *Passive Nondestructive Assay of Nuclear Materials*, US NRC Publication NUREG/CR-5550 (1991).
4. T. Gozani, *Active Nondestructive Assay of Nuclear Materials*, US NRC Publication NUREG/CR-0602 (1981).
5. S.T. Hsue, J.E. Stewart, P. M. Rinard, and G. Butler, "Guide to Preparation of Nondestructive Assay Calibration Standards," Los Alamos National Laboratory Report in preparation (1996).
6. "Standard Guide for Preparation of Working Reference Materials for Use in the Analysis of Nuclear Fuel Cycle Materials", American Society For Testing and Materials, Designation C1128-89, ASTM 100 Barr Harbor Dr., West Conshohocken, PA 19428.
7. S. Guardini, G. Guzzi, F. Mousty, S. Baumann, E. Kuhn, and P. De Regge, "Quality Control Provisions Applied in the Preparation and Characterization of Pu-Bearing PERLA Standards," Institute for Safety Technology, PERLA Safeguards Performance Laboratory, CEC report EUR-13038-EN (1990).
8. New Brunswick Laboratory, U.S. Department of Energy, 9800 South Cass Avenue, Argonne, IL 60439-4899.
9. S. -T. Hsue, S.M. Simmonds, V.L. Longmire, and S.M. Long, "Design and Fabrication of SGS Plutonium Standards," in Fourth International Conference on Facility Operations-Safeguards Interface (American Nuclear Society, La Grange Park Illinois, 1991), pp. 410-413.
10. P. Matussek, "Accurate Determination of the  $^{235}\text{U}$  Isotope Abundance by Gamma Spectrometry: A User's Manual for the Certified Reference Material EC-NRM-171/NBS-SRM-969," Insitutut für Kernphysik report KfK 3752, Kernforschungszentrum, Karlsruhe, Federal Republic of Germany (1985).
11. J. L. Parker and M. Brooks, "Accurate, Wide-Range Uranium Enrichment Measurements by Gamma-Ray Spectroscopy: I. Characterization of Enrichment Standards; II. Demonstration of Enrichment Measurement Capability," Los Alamos National Laboratory Report LA-11277-MS (September 1988).
12. Ray Gunnink, "MGA: A Gamma-Ray Spectrum Analysis Code for Determining Plutonium Isotopic Abundances, Vol. 1: Methods and Algorithms," Lawrence Livermore National Laboratory Report UCRL-LR-103220, Vol. 1 (April 1990).
13. Thomas E. Sampson, George W. Nelson, Thomas A. Kelley, "FRAM: A Versatile Code for Analyzing the Isotopic Composition of Plutonium from Gamma-Ray Pulse Height Spectra," Los Alamos National Laboratory report LA-11720-MS (December 1989).
14. CBNM Certified Nuclear Reference Material 271, Certificate of Analysis, Commission of the European Communities, Joint Research Center, Central Bureau for Nuclear Measurements (January 1989).
15. J. Morel, B. Chauvenet, M. Etcheverry, S. Guardini, R.J.S. Harry, G. Wells, "Final Results of the PIDIE Inter-comparison Exercise for the Plutonium Isotopic Determination by Gamma Ray Spectrometry," Proceedings of the 13th Annual Symposium on Safeguards and Nuclear Material Management, ESARDA (May 1991).

16. F.. Hsue, S.M. Long, S. -T. Hsue, and M.C. Miller, "Design and Fabrication of Uranium Drum Standards," *Nucl. Mat. Manage.* XXII (Proceedings Issue), 940-944 (1993).
17. F. Hsue, P.A. Trupp, T. Wilson, E. Vigil, D. Knobloch, and M. Krick, "AWCC Uranium Can Standards Fabrication and Documentation," Los Alamos National Laboratory Report NMT4-STD1-92 (January 1992).