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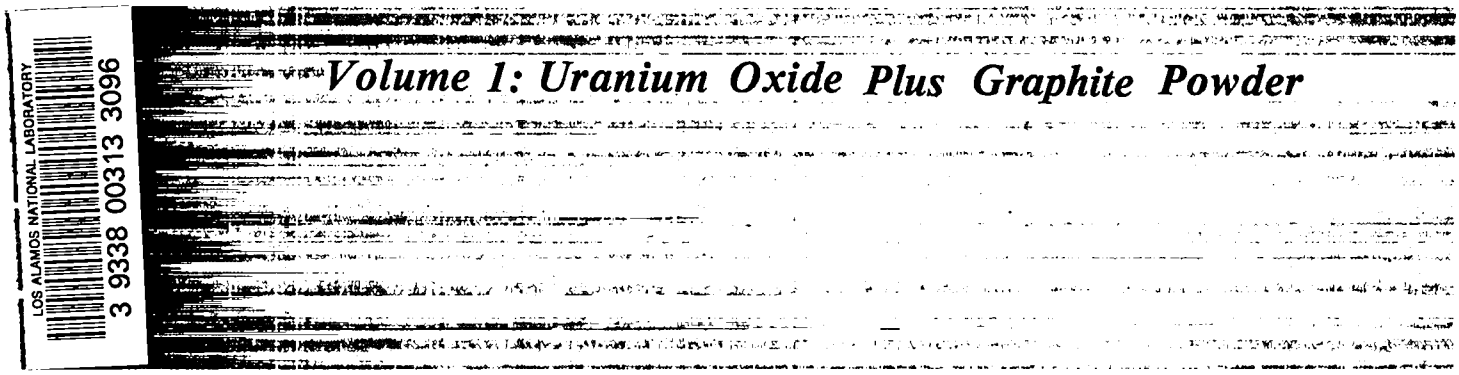
Reference Materials for Nondestructive Assay of Special Nuclear Material



Volume 1: Uranium Oxide Plus Graphite Powder

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REFERENCE MATERIALS FOR NONDESTRUCTIVE ASSAY OF SPECIAL NUCLEAR MATERIAL

Volume 1: Uranium Oxide Plus Graphite Powder

by

J. K. Sprinkle, R. N. Likes, J. L. Parker, and H. A. Smith

ABSTRACT

This manual describes the fabrication of reference materials for use in gamma-ray-based nondestructive assay of low-density uranium-bearing samples. The sample containers are 2-ℓ bottles. The reference materials consist of small amounts of UO_2 spread throughout a graphite matrix. The ^{235}U content ranges from 0 to 100 g. The manual also describes the far-field assay procedure used with low-resolution detectors.

PART 1

PRODUCTION OF REFERENCE MATERIALS FROM URANIUM OXIDE PLUS GRAPHITE POWDER

I. INTRODUCTION

A. Role of Reference Materials in Nondestructive Assay

Reference materials provide two functions in nondestructive assay (NDA). They are used to calibrate NDA instruments and to verify the constancy of the calibrations. Traceability is important only for the calibration aspect. Constancy of the calibration can be verified with any material that provides a stable, consistent signal. Clearly, a calibration is misleading if the reference material loadings are not well known. However, the loading values need not be known to much greater accuracy than that achievable by the assay. If a reference material is known to one-fourth the expected measurement uncertainty, it contributes little to the overall uncertainty of the measurement. (The investigation of systematic effects has more rigorous requirements on the accuracy requirements for the reference materials.)

The reference materials should represent the samples in aspects to which the particular measurement technique is sensitive. However, contrary to popular thought, exact representation is not necessary if the measurement physics is well understood and properly applied. For example, for transmission corrections, the reference materials must have transmissions for which a correction can be made accurately, but they do not need precisely the same transmission as each sample.

The second function (that of verifying the constancy of the instrument's calibration) merely requires a stable reference material. Because the technique is nondestructive, the same sample can be used repeatedly to verify the same instrument response. It is much easier to make stable reference materials than to ensure that multiple reference materials are accurate and appropriate in all necessary ways.

B. Measurement Applications

The measurements addressed in this manual concern the bulk assay of uranium-bearing materials using transmission-corrected gamma-ray assay techniques. The emphasis is on samples of low-density material with uniform uranium dispersion. The transmission of a 185.7-keV gamma ray through the sample must be finite and measurable. The far-field low-resolution technique described in Part 2 becomes difficult to use at transmissions below approximately 5%.

Changing to a high-resolution detector and a different transmission source allows this technique to be extended to transmissions below 1%.

As the sample transmission approaches zero, the 185.7-keV assay changes character significantly and a quantitative assay becomes impossible. The operator may be able to use an enrichment measurement plus a sample weight and an assumption of uniformity to yield a ^{235}U assay. The high-energy gamma rays from the ^{238}U daughter, ^{234m}Pa, may be used if (1) the material is more than a hundred days old (that is, if more than a hundred days have elapsed since the protactinium was separated), (2) the count rate is sufficient, and (3) the sample composition is sufficiently uniform. But the transmission-corrected 185.7-keV assay is meaningless for those samples that have a transmission of zero at 185.7 keV.

C. General Character of the Selected Reference Materials

Both the uranium loadings and the matrix were chosen to be low density, allowing for accurate transmission measurement and, in turn, accurate transmission correction. The nominal ^{235}U loadings (10, 15, 50, 75, 100 g) cover the range of expected sample loadings. Therefore, the reference materials have sufficient material to allow for good counting precision, and reasonable transmissions are obtained. The nominal ^{238}U loadings (10, 15, 50, 75, 100 g) exceed the largest expected ^{238}U sample, allowing for a more precise calibration. Most of the samples will be in 2-ℓ bottles; consequently, 2-ℓ bottles were chosen for the reference material containers. Other containers may require different corrections, as discussed in Part 2.

II. PREPARATION

A. Desired Characteristics

The reference materials do not need to resemble the sample closely,[1] but the calibration will be easier if they do. Reliable corrections must be applied to account for the sensitivity of the measurement technique to certain characteristics. The important parameters for a passive measurement technique are the distance that the gamma radiation must travel to the detector, the gamma-ray energy, and the attenuation it suffers. Therefore, computation of a correction for the gamma-ray attenuation requires that the reference material

(and sample) be homogeneous; lumps of gamma emitters or absorbers can decrease the amount of gamma radiation emitted from the reference material with no indication to the user from the bulk transmission measurement. In addition, the reference material must be stable with respect to settling and migration of the special nuclear material.

If the reference materials and samples are the same size and packaged in similar containers, the same correction factor (CF) expression applies to both. Otherwise, a different CF is applicable even when the transmissions are identical. The CF explicitly corrects for different transmissions and different sample geometries. The CF can be a significant source of uncertainty in the assay if the transmission is very low. Consequently, a lower limit applies for permissible transmissions.

It is more important that the reference materials verify the calibration and operation of the instrument than that they span the range of representative loadings. Similar loadings for the sample and reference materials may be used, but are not required. In many cases, adequate measurement precision obtained from high loadings is more important than the use of similar loadings.

B. Production Using Fine-Mesh Powders

Our initial approach consisted of mixing fine U_3O_8 powder with graphite flour. We assumed that sufficiently small particles would compact rather firmly and would not tend to stratify or migrate. Although our assumption was true, the small particle sizes introduced other difficulties.

The U_3O_8 powder contained 84.78 wt% uranium. Isotopic analysis showed it to contain 97.3 wt% ^{235}U. Figure 1 shows the particle size distribution. The graphite flour was finely ground spectroscopic-grade material.

The U_3O_8 powder was heated to 300°C for 2 h to drive off the water, then weighed into tared bottles; approximately 1 kg of graphite flour was poured on top. The bottles were filled only halfway in order to allow plenty of space for mixing. The bottles were then sealed and the verification/mixing procedure was begun.

The first sealed bottle, containing a fully stratified nominal 50 g of ^{235}U, was assayed, then mixed, then assayed again. This mixing/assaying cycle was repeated several times until the sample material was as thoroughly mixed as possible. Figure 2 shows selected ^{235}U profiles in the reference

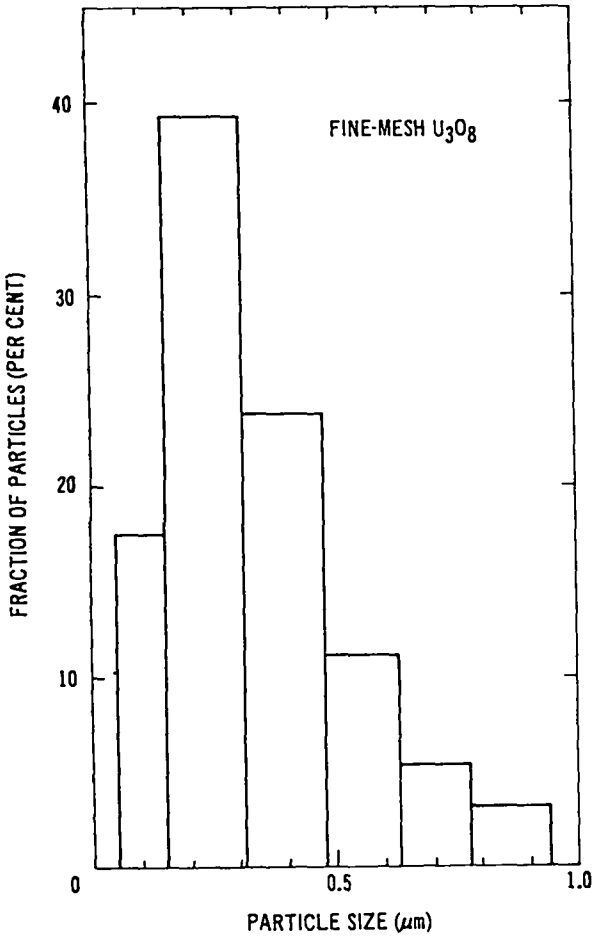

Fig. 1. Particle size distribution for the fine-mesh U_3O_8.

material as the mixing progressed; the profiles were obtained with transmission-corrected segmented gamma-ray scan (SGS) assay.[2] The four profiles, labeled A through D in Fig. 2, yielded the assay results shown in Fig. 3. The assays were performed with the SGS technique and far-field transmission-corrected assay procedures using NaI (low-energy resolution) and germanium (high-energy resolution) gamma-ray detectors. The measurement setups were calibrated with the reference materials described in Sec. III.B. The assay results show that nonuniformities in the sample material, compared with the uniform distribution in the reference materials, can cause drastic underestimation of the assay values. The SGS technique is understandably less vulnerable to this problem, but inaccuracies are still evident for highly nonuniform mixtures. These results point out both the importance of proper axial positioning of the sample material and the value of some knowledge (and even control) of the material distribution in unknown samples (for example, fill heights).

After the assays corresponding to profile D were completed, problems with these reference materials began to appear. The NDA techniques specified in the preceding paragraph yielded assays that were approximately 5% lower than the reported analytical values. In addition, successive assays after extensive mixing attempts sometimes yielded profiles that were less uniform than profile D. It became obvious that large lumps of higher density uranium loadings were immersed in a more dilute uranium-graphite mixture. When it became clear that these lumps were shifting around without breaking up, the reference materials

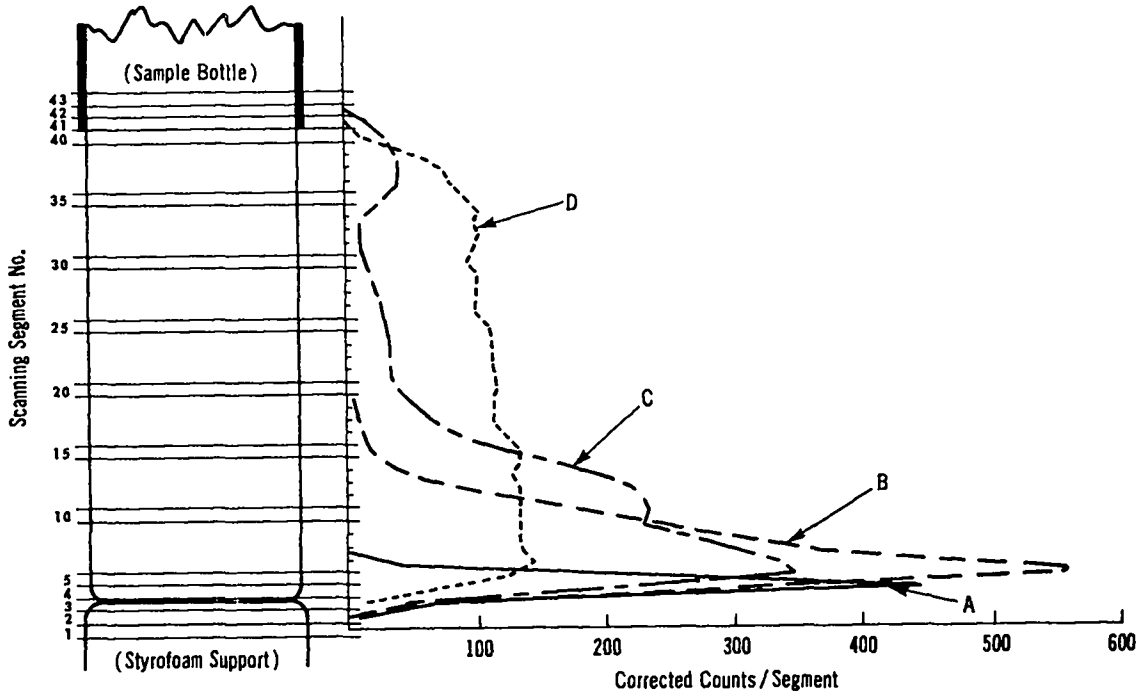

Fig. 2. SGS profiles of the U_3O_8 plus graphite powder reference material as a function of mixing: Profile A (the original) shows the U_3O_8 on the bottom of the bottle; profiles B, C, and D show the U_3O_8 spreading through the bottle as it is mixed.

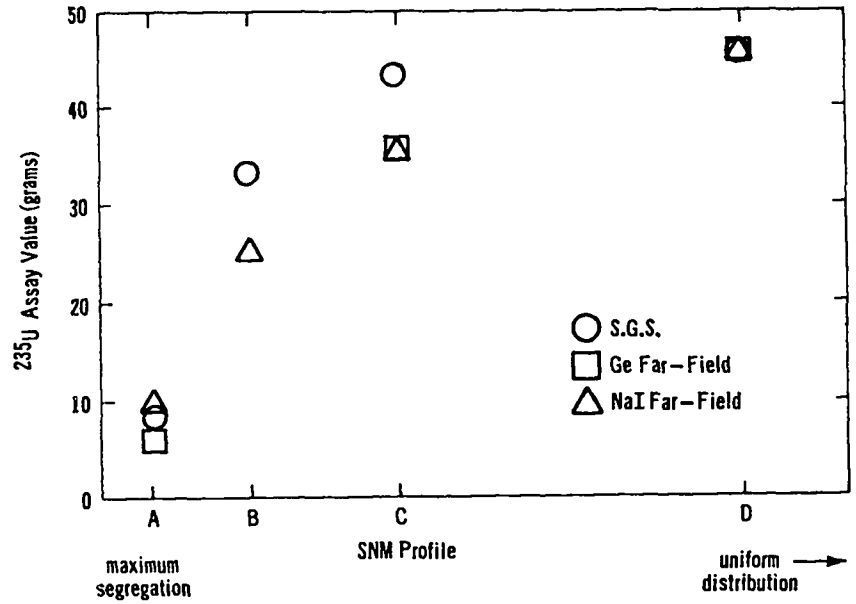

Fig. 3. Uranium-235 assay corresponding to the four profiles in Fig. 2. Three assay systems were used; for poorly mixed materials, the SGS results were usually closer to the expected values.

were opened and the material was blended in a 2-qt Patterson-Kelley twin-shell blender equipped with an intensifier bar. Figure 4 shows radiographs before and after this blending. Although the blending did not completely break up the lumps, the uniformity of the ^{235}U distribution was somewhat improved. However, the presence of the remaining lumps caused the gamma-ray assays to be approximately 2% below the values determined during preparation of the reference materials. Consequently, the reference materials were discarded.

Fig. 4. Radiographs of the U_3O_8 plus graphite powder reference material. The left radiograph is after intensified blending; the right is before.

Further investigation showed that small (diameter <2 μm) particles are susceptible to clumping, perhaps as a result of electrostatic forces. This problem can be alleviated either by wetting the particles or by using larger particles that are not as prone to clumping.

C. Production Using Wet Blending and Larger Particle Sizes

Our second approach was to make a well-dispersed mix of UO_2 powder and graphite flour and to keep the material dispersed by adding an organic binder.[3] To obtain a uniform mixture of the binder with the dry ingredients, the binder was added with a volatile solvent. The volatile solvent was then removed.

The UO_2 powder contained 87.8 wt% uranium. Isotopic analysis showed the uranium to contain 52.22 wt% ^{235}U. A standard densified powder was used, which was relatively free flowing and contained a minimum of fines.* Figure 5 shows the particle size distribution. Densified UO_2 powder tends to disperse uniformly without excess formation of agglomerates. Fine powder (diameter <2 μm) tends to agglomerate and these agglomerates are very difficult to break up even with intensive mixing. The graphite flour was reactor grade having particles

*Fines are particles that are considerably smaller than the majority of the particles.

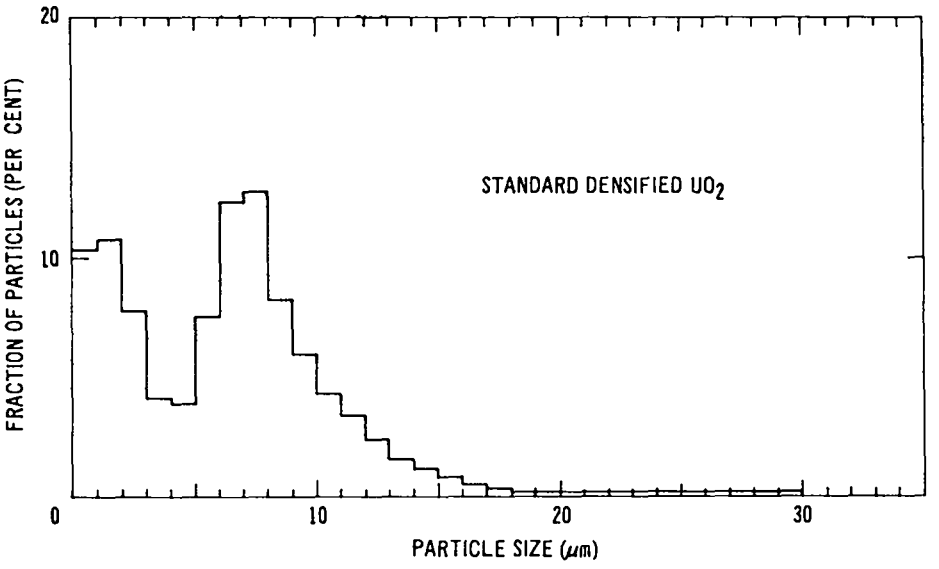

Fig. 5. Particle size distribution for the densified UO_2.

less than 60 mesh (diameter <250 μm). The flour, supplied by Great Lakes Carbon Company, Inc., was made from purified stock having a density over 1.65 g/cm^3. The organic binder was commercial camphor and the solvent was Chlorothene.*

A 2-qt Patterson-Kelley twin-shell blender equipped with intensifier bar and liquid addition apparatus was used to mix the constituents. The blender was not large enough to hold the 2 ℓ of mixture required, so the mixture was made in two parts. First, the graphite flour and UO_2 were dry blended, using the intensifier bar, for 15 min. The camphor was dissolved in Chlorothene and slowly added to the blender through the liquid addition apparatus for approximately 10 min. The blending was continued for an additional 5 min and the blender was emptied. The second part of the blend was then made in the same manner. Both batches were hand mixed, then rubbed through a 14-mesh sieve and placed in the 2-ℓ polyethylene bottle. It was necessary to tap the bottle on the bench top to settle the material to the desired level. The loaded bottle was placed in a circulating air oven, heated to 60°C, and held at this temperature for 40 h. The lid was not on the bottle for this operation, but was replaced by a loose-fitting piece of aluminum foil. After the material was dried, the bottle was placed in a vacuum oven, again with a loose-fitting

*Trademark for inhibited 1,1,1-trichloroethane.

aluminum foil cover. The vacuum was applied gradually over 8 h, then remained overnight at approximately 0.58 m of mercury. This operation was performed at room temperature. The bottle was then closed and sealed. Figure 6 is a radiograph of one of these reference materials. The clumping of the U_3O_8 shown in Fig. 4 is noticeably absent in the densified UO_2 material. When the blending operation was complete for each uranium loading, the equipment was thoroughly cleaned and the material was placed in the bottle. The equipment was then washed with acetone, and the washings were collected in a pan. The acetone was subsequently evaporated, and the residue left in the pan was weighed and factored for uranium content. Because the overnight vacuum treatment, necessary to remove the Chlorothene from the mixture, also removed some camphor,* it was not possible to obtain an accurate weight balance. It was assumed that all of the uranium placed in the blender ended up either in the bottle or in the measured residue washed from the equipment.

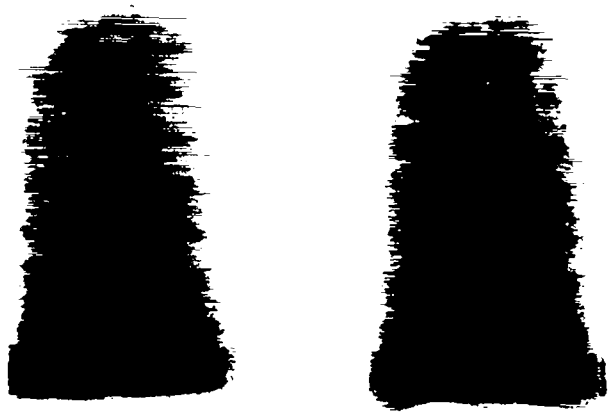

Fig. 6. Radiographs of one of the densified UO_2 plus graphite powder reference materials.

Tapping the bottle to get the packed material to the proper level resulted in a slight density gradient in the bottle contents. After the contents were dried, there was some loose material at the top of the bottle and some of the material in the bottle shrank away from the sides.

Further investigations demonstrated that wet blending is not a necessary part of this procedure. A dry mixture of standard densified UO_2 with graphite flour is easy to mix and is stable against segregation after mixing. Dry mixtures can be traced through accurate weighing.

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*To determine how readily the camphor was evaporated in the environment of the vacuum oven, a known quantity of graphite flour was placed in a bottle along with a known amount of camphor dissolved in Chlorothene. These ingredients were mixed in the bottle, with care taken not to spill any contents. The mixture was then dried, using the same conditions used on the bottles containing densified UO_2. Twenty percent of the camphor was evaporated.

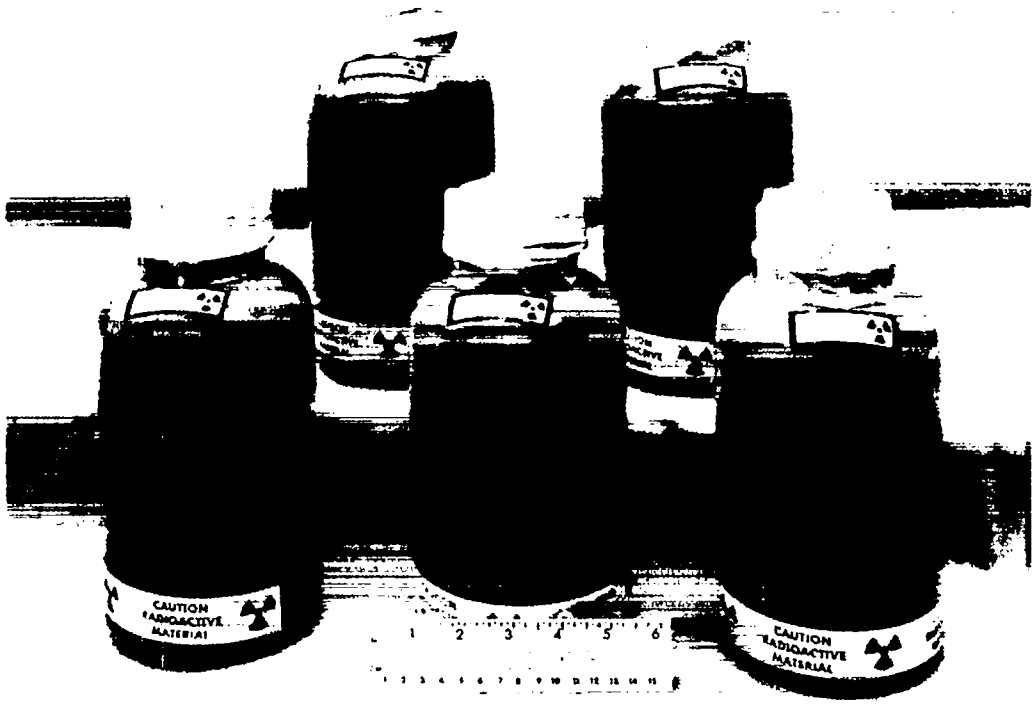

Fig. 7. Densified UO_2 plus graphite powder reference materials.

D. Preparation Results

Five new reference materials are shown in Fig. 7. They demonstrate the required homogeneity and stability against segregation. These reference materials can be handled extensively, however severe mishandling might create air pockets that could bias the assay. Their transmissions at 185.7 keV cover the range of 0.02 to 0.17. Table I gives the isotopic analysis content.

Table II summarizes the estimated uranium loadings for each bottle. The second column lists the amount of densified UO_2 at the beginning of the wet blending process. The third column adjusts these values according to the amount of material found in the equipment washings and cleanup. The fourth column converts these numbers to ^{235}U. The equipment washings and rags for each bottle were packaged separately

TABLE I

URANIUM ISOTOPIC DISTRIBUTION

Isotope	wt %
234	0.517
235	52.22
236	0.671
238	46.59

TABLE II

URANIUM CONTENT OF THE REFERENCE MATERIALS

ID	UO_2 in Blenders (g)	Estimated UO_2 in Bottles (g)	Estimated ^{235}U in Bottles (g)	Adjusted ^{235}U in Bottles (g)
Q1-HS-10	22.08	21.9	10.04	10.04
Q1-HS-15	34.04	33.8	15.49	15.49
Q1-HS-50	110.4	109.7	50.29	50.29
Q1-HS-75	165.6	164.3	75.33	75.73
Q1-HS-100	220.8	218.2	100.02	99.62

and assayed nondestructively for ^{235}U. Two low-resolution gamma-ray techniques and one active neutron technique were used. In two of the five loadings, a significant difference (0.4 g) was found when the low-resolution gamma-ray assay values were compared to the cleanup-weight tag values. The fifth column incorporates these adjustments. An estimate of the accuracy of these values is 1 to 2%. Figure 8 shows a proposed label for identifying the new reference materials.

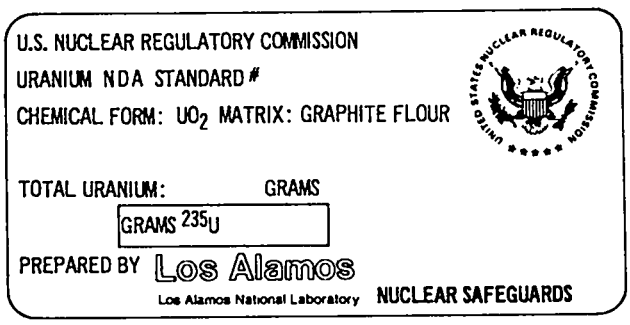

Fig. 8. Proposed label for densified UO_2 plus graphite powder reference materials.

III. VERIFICATION

A. Introduction

Because of their sensitivity to different characteristics, several gamma-ray assay techniques were used to verify the uranium content of the new reference materials. In addition, homogeneity, an important property for the proposed assay technique, was verified. The radiographs in Fig. 6 demonstrated a lack of the clumping that plagued the initial attempt. Although neutron-based assays tended to confirm the relative values, they were

sensitive to the hydrogen content and calibration was not possible. Reference 4 provides a detailed explanation of gamma-ray assay techniques.

B. Calibration Reference Materials

Repackaged uranium oxide plus graphite powder reference materials, belonging to the Safeguards Assay Group at Los Alamos National Laboratory, were used to calibrate the nondestructive assays for ^{235}U. These Los Alamos reference materials are shown in Fig. 9. The containers are approximately two-fifths full in order to allow the user to mix the contents if desired. In the last 10 years, only one of the reference materials required mixing. The container with 200 g of uranium was mixed only to decrease the density of the contents after they settled and compacted. The long-term stability of these reference materials is well known; they have never demonstrated the inclination to stratify or separate. Their loadings have been verified several times to

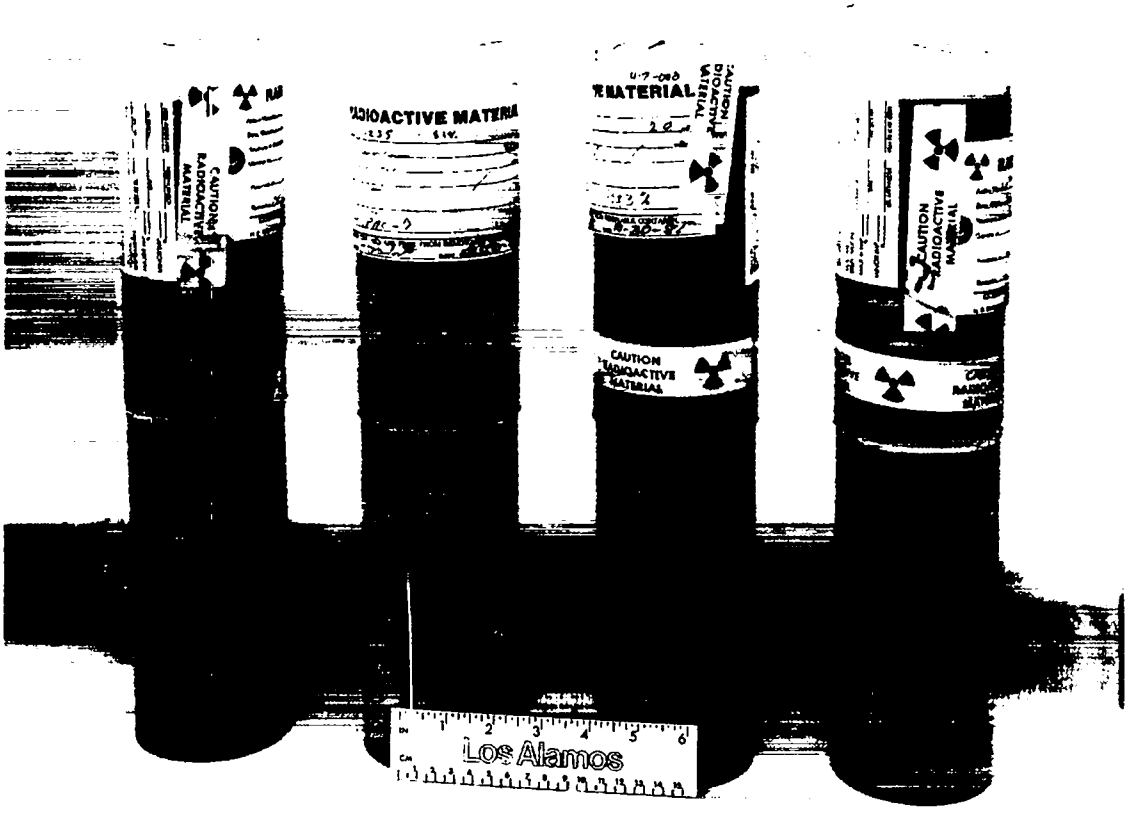

Fig. 9. Los Alamos reference materials used to calibrate the ^{235}U verification assay equipment.

the precision of the verification measurements. They have been compared to solution standards and thin foils.[1]

The assays for the ^{238}U verification were calibrated with two depleted uranium disks, approximately 6 cm in diameter by 0.5 or 1.0 cm thick. The uranium metal was cleaned, weighed, and then coated with a known thickness of nickel. Because the disks were several years old, equilibrium had been established between ^{238}U and the ^{234m}Pa daughter.

C. Transmission-Corrected Segmented Gamma Scans (High Resolution)

The correct operation of an SGS is well documented.[2] The advantage of viewing a sample in segments is that it allows the user to investigate the sample homogeneity segment by segment. The technique has its limitations; although, as Fig. 2 demonstrates, certain types of nonuniformities can become obvious. Figure 10 shows the profiles for the five new reference materials. The error bar on each segment assay (data point) is the statistical uncertainty associated with the assay of that particular segment. The profiles show slight (<15%) density gradients from top to bottom of the containers, as a consequence of the stickiness of the mixture and the bottle-filling procedure. Although the

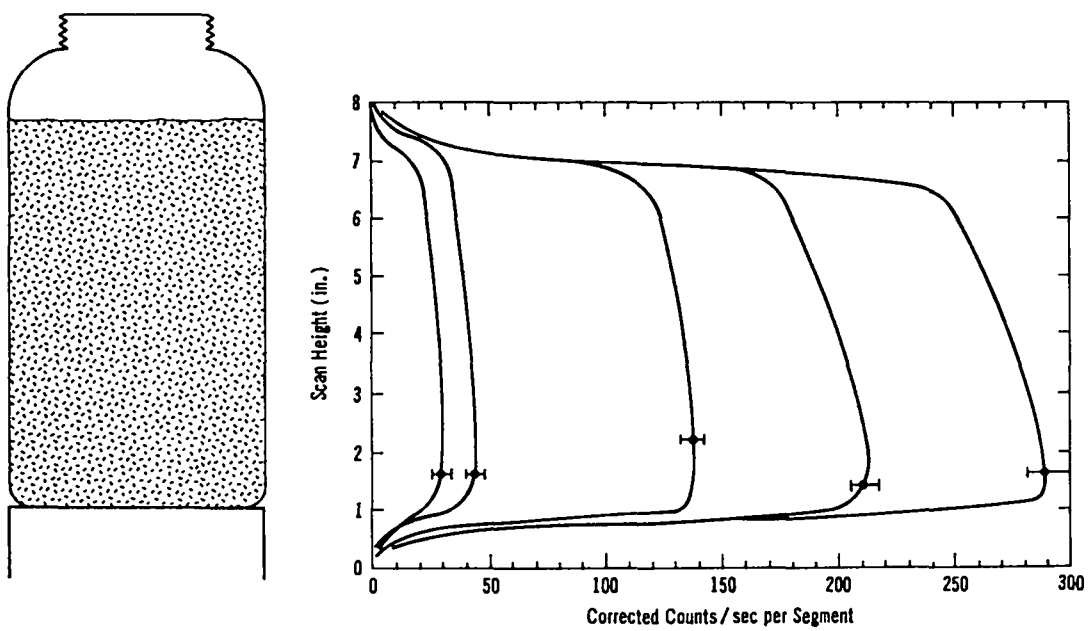

Fig. 10. Profiles for the new reference materials obtained from the SGS measurements. The error bars correspond to 1 standard deviation for a single segment, based on counting statistics.

presence of density gradients is undesirable, the error it contributes to these gamma-ray-based assay techniques is small (<1% in the worst case).

D. Far-Field Low-Resolution Spectroscopy

The object of a far-field assay is to make the sample-to-detector distance much larger than the sample dimensions. If these quantities have a ratio of 10:1, the sample can be considered a self-attenuating point source to a very good approximation. This is to be contrasted with the segmented scanning technique that requires the detector collimator to be as close to the sample as possible (for example, 1.0 cm). Part 2 describes the far-field configuration used with a low-resolution detector. The transmission source uses the same gamma-ray energy as the sample because of the low energy resolution of the detector. The transmission source is a slit source; consequently, an average transmission for the bottle is obtained, instead of the transmission through a very small fraction of the bottle.

For the 185.7-keV measurements for ^{235}U, the source-to-detector distance was 40 cm. The detector was a 7.6-cm by 7.6-cm NaI, and the amplifier was gain-stabilized. The Compton continuum under the peak was estimated by using a background region above the peak.

For the 1-MeV measurements for ^{238}U (actually for the ^{234m}Pa daughter of ^{238}U), the source-to-detector distance was 65 cm. The detector was a 12.7-cm by 12.7-cm NaI, and the amplifier was gain-stabilized. Transmission measurements were obtained with the high-resolution system described below. The Compton continuum under the peak was estimated by first subtracting a room background, then using a background region on each side of the peak. This 12.7-cm by 12.7-cm setup was also used to observe the 2.6-MeV gamma ray from a daughter of $^{232}U(^{208}Tl)$. No absolute calibration was determined; however, the attenuation at 2.6 MeV is identical for the five reference materials, and there is a very low background at that energy.

Because of the low energy resolution of NaI detectors, these assays are not as reliable as high-resolution assays. Small interferences from gamma rays with energies close to the gamma ray of interest can be impossible to resolve and can bias an assay significantly. It is also a nontrivial matter to determine the Compton continuum under a peak.

E. Far-Field High-Resolution Spectroscopy

The addition of a high-resolution detector significantly improves the quality of a far-field assay. The drawback is a loss in detection efficiency, especially at high energies (>600 keV). However, the increased ability to resolve interferences and to accurately determine peak areas often offsets the loss in efficiency.

This setup had a sample-to-detector distance of 80 cm. The detector was a large coaxial Ge(Li). A ^{169}Yb source was used to measure transmissions at 177 and 198 keV, which were interpolated to 185.7 keV for the ^{235}U assay. Both a ^{226}Ra source and the ytterbium source were used to measure transmissions at 295, 308, 352, 609, 768, 934, 1120, 1238, 1378, 1509, 1730, and 1764 keV; these were interpolated to 1001 keV for the ^{238}U assay. The external point source is much more intense and can be used at several discrete positions, thus yielding a more accurate transmission more rapidly than the uranium source with a slit collimator.

F. Verification Results

As soon as the verification exercises began, an inconsistency between one of the tag values and the corresponding NDA value became apparent. The worst aspect of this inconsistency was that the tag value was smaller. Except for statistical fluctuations, gamma-ray-based NDA tends to underestimate the ^{235}U content if it is in error, not overestimate it. As a result, the verification procedures were subjected to stricter criteria.

The low-resolution far-field assay of ^{235}U is generally believed to have an accuracy of a few percent for good samples. These results are listed in Table III, but are not included in the final analysis because of their lack of accuracy. The low-resolution far-field assay of ^{238}U was even less accurate, mainly because of the difficulty in determining appropriate backgrounds when the signal-to-noise ratio was 1 or less. The 2.6-MeV gamma ray from ^{232}U was used to measure the relative loadings because no absolute calibration was possible. The ratios have an accuracy of 1 to 2%. A conservative estimate of the accuracy of the high-resolution far-field assay for ^{235}U is 1%. Because the high-resolution far-field assay of ^{238}U suffered background and low count rate problems, only the highest loadings were assayed. The accuracy is estimated to be 1 to 2% for these measurements. The SGS can provide assays to better than 1% for these demonstrably uniform samples. Table III lists the

TABLE III

VERIFICATION ASSAY RESULTS FOR ^{235}U

ID	Adjusted ^{235}U (g)	SGS 235U (g)	Far-Field ^{235}U High Resolution (g)	Average (g)	Far-Field ^{235}U Low Resolution (g)
Q1-HS-10	10.04	9.89 ± 0.12 10.11 ± 0.07	10.17 ± 0.04	10.07	10.8 ± 0.1
Q1-HS-15	15.49	15.42 ± 0.14 15.40 ± 0.10	15.55 ± 0.06	15.48	16.1 ± 0.1
Q1-HS-50	50.29	50.12 ± 0.20 50.52 ± 0.40 50.76 ± 0.34	51.20 ± 0.20	50.65	54.6 ± 1.2
Q1-HS-75	75.73	75.69 ± 0.38 75.91 ± 0.38	75.15 ± 0.30	75.56	76.2 ± 2.8
Q1-HS-100	99.62	103.55 ± 0.35 103.64 ± 0.41	103.84 ± 0.42	103.72	Transmission too low

results of the verification. The uncertainties listed in the table are the statistical precisions estimated from counting statistics. The accuracies are those quoted above.

For the four reference materials with the least amount of ^{235}U, an unweighted average of the SGS results was averaged with the high-resolution far-field value and the adjusted value to obtain the average result. For the Q1-HS-100 reference material, the adjusted value was not included in the average. All averages were unweighted. The uncertainty in these averages was estimated to be less than 0.5%.

Gamma-ray-based assays tend to be low if they are in error. Table IV lists the ratios of the gamma-ray results to the adjusted estimated loadings. In four of the reference materials, the gamma-ray-based assay results agree

TABLE IV

RATIO OF GAMMA-RAY-BASED ASSAY RESULTS TO ADJUSTED ESTIMATED URANIUM LOADINGS

ID	Gamma-Ray Average/ Adjusted Estimated Loading
Q1-HS-10	1.004
Q1-HS-15	0.999
Q1-HS-50	1.011
Q1-HS-75	0.997
Q1-HS-100	1.041

very well with the adjusted values. However, the largest loading shows a significant difference. An error in the adjusted estimated values could have originated during extensive handling in preparation of the reference materials or from analyses of mass spectrometry or grams uranium per gram material. The chemical analyses were common to all five reference materials, however the handling was independent, perhaps resulting in an error for one of the bottles. An error in the gamma-ray-based assays could only originate from nonhomogeneities or an incorrect calibration. The radiographs show no evidence of nonuniformities that could cause these differences, nor do the SGS measurements. In addition, the differences in counting geometry between the SGS and far-field measurement configurations would cause them to respond differently to nonuniform samples (see discussion in Sec. V.A.).

If the credentials of the NDA calibration standards are questioned, their use can be eliminated. Consider the ratios in Table V of the assay of Q1-HS-75 to the assay of Q1-HS-100. (These are the reference materials containing a nominal 75 and 100 g ^{235}U, respectively). The use of a ratio eliminates many common factors from consideration that could bias the NDA assay. Two of these factors are the geometry and the calibration. Three different isotopes were assayed using widely different gamma-ray energies that display widely different attenuation properties. The 185.7-keV gamma ray has transmissions of 2 to 17% in the five samples; the 1-MeV gamma ray has transmissions of 39 to 43% in the five samples; and the 2.6-MeV gamma ray has essentially the same transmission for all five samples. The far-field and SGS assays have geometries with D/R

ratios of 10 and 2, respectively, where D is the sample-to-detector distance and R is the sample radius. Their respective response to nonuniform loadings would differ widely, unless the uranium consisted of small lumps. However, that nonuniformity would cause the gamma-ray assays to be low rather than high. The fact that the four ratios agree so well with one another, yet disagree with the estimated loadings, is fairly substantial evidence that the ratio of uranium in Q1-HS-75 and Q1-HS-100 is not that reported in the estimates. Based on this conclusion, the tag value for the Q1-HS-100 reference material will be the average gamma-ray value; this tag value is also consistent with the intended use of this reference material. The transmission through Q1-HS-100 at 186 keV is too small for low-resolution assays, however the homogeneity that it exhibits makes Q1-HS-100 an excellent candidate for use as the transmission source.

TABLE V

RATIOS OF ^{235}U IN Q1-HS-75 AND Q1-HS-100

Original estimate	0.7529
Adjusted estimate	0.7602
SGS (^{235}U)	0.7317
Far-field high resolution (^{235}U)	0.7237
Far-field low resolution (^{232}U)	0.7413
Far-field high resolution (^{238}U)	0.7235
Average of four NDAs	0.7301 ± 0.0084

PART 2

USE OF REFERENCE MATERIALS
CONSISTING OF URANIUM OXIDE PLUS GRAPHITE POWDER

IV. INTRODUCTION

The densified UO_2 plus graphite reference materials were developed for use in the far-field low-resolution assay procedure. They are also appropriate for more sophisticated gamma-ray techniques using high-resolution detectors or segmentation. Part 2 of this manual emphasizes the low-resolution far-field technique; however, where appropriate, the manual recommends future implementation of improvements that can be achieved with more sophisticated procedures and equipment.

Far-field low-resolution assay can be used with low-density uranium-bearing materials, subject to several restrictions. The samples (and reference materials) should have similar fill heights and container sizes. They should be homogeneous and not contain lumps of ^{235}U. They must have measurable transmissions at 185.7 keV (typically >5%). If the samples do not fulfill these requirements, incorrect assays usually result. The amount of bias can be related (but not simply) to how poorly the samples fulfill these requirements. The more advanced techniques are less susceptible to some or all of the biases.

An understanding of the measurement physics is essential. Good standards do not guarantee good assays. The assay technique must be properly applied to appropriate samples.

V. FAR-FIELD LOW-RESOLUTION ASSAY PROCEDURE

A. Assay Configuration

In the assay configuration shown in Fig. 11, the detector should be shielded from all sources of radiation except the sample and the transmission source. A thickness of 1.3 cm of lead is sufficient shielding for 185-keV gamma rays. Gamma rays of higher energy can usually be reduced to acceptable intensities by 5.1 cm of lead, however 1-MeV gamma rays may require 20 cm of lead shielding. Note that the detector is sensitive to radiation from all directions. A 0.16-cm-thick cadmium filter (placed between the detector and sample) is helpful in reducing low-energy background, such as uranium or lead x rays.

The detector axis, the sample center, and the point transmission source should all lie on the same axis. If a line source is used, it should be

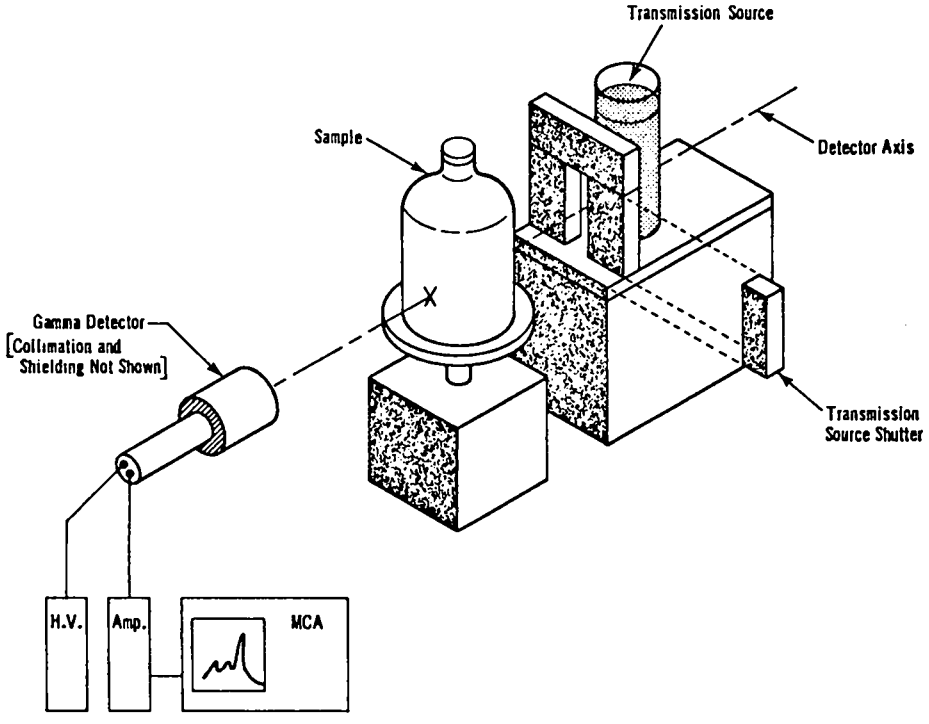

Fig. 11. Low-resolution far-field assay configuration.

shorter than the sample height (approximately one-half to two-thirds the sample height). In addition, it should be offset to preferentially interrogate the lower, more densely compacted portion of the 2-ℓ bottle containing the sample. If the sample-to-detector distance is D and the sample radius is R, D/R should be 7 or larger, to reduce the assay dependence on sample size. The correction factors in Sec. V.B are given for D/R = 7, 10, and 15. Sample height is also a consideration. For a sample half-height of Z, Table VI lists the variation in detector count rate between a source at the center of the sample, CR(0), and a source at the top of the sample, CR(Z).

The samples should be rotated because their homogeneity is unknown. Table VII lists the ratios of the average counter response to a source on the radius R, CR(R), to the response of a source at the sample center, CR(0), for the rotating and nonrotating cases (assuming the sample rotates at least 10 revolutions during the count).

TABLE VI

COUNT RATE VARIATION AS A FUNCTION OF SAMPLE HALF-HEIGHT

D/Z	CR(Z)/CR(0)
2	0.80
3	0.90
4	0.94
5	0.96

TABLE VII

THE EFFECT OF SAMPLE ROTATION ON COUNT RATE

D/R	Rotating CR(R)/CR(0)	Nonrotating CR(R)/CR(0)
2	1.33	4.00
7	1.02	1.36

Figure 12 shows details of the sample and the transmission source. The low-resolution system requires the use of the same energy gamma ray for both the assay peak and the transmission source. A line source works best, approximately 2 cm wide (if the sample is a 2-ℓ bottle) and one-half to two-thirds the sample fill height. A good candidate for this type of transmission source is the reference material with the highest loading, Q1-HS-100 (placed behind a few lead bricks). The transmission source must have a uniform distribution of uranium and it should not be allowed to shine over, around, or under the sample. The capability of repositioning the transmission source to give the same intensity or of blocking it with a shutter is extremely important.

Reliable assays can be accomplished with single channel analyzers, but multichannel analyzers allow more flexibility, give a better indication of whether problems are arising, and are easier to set up. Stabilization of the system is required, despite the fact that broken stabilizers could well be the most difficult problem to troubleshoot. Photomultipliers are not sufficiently

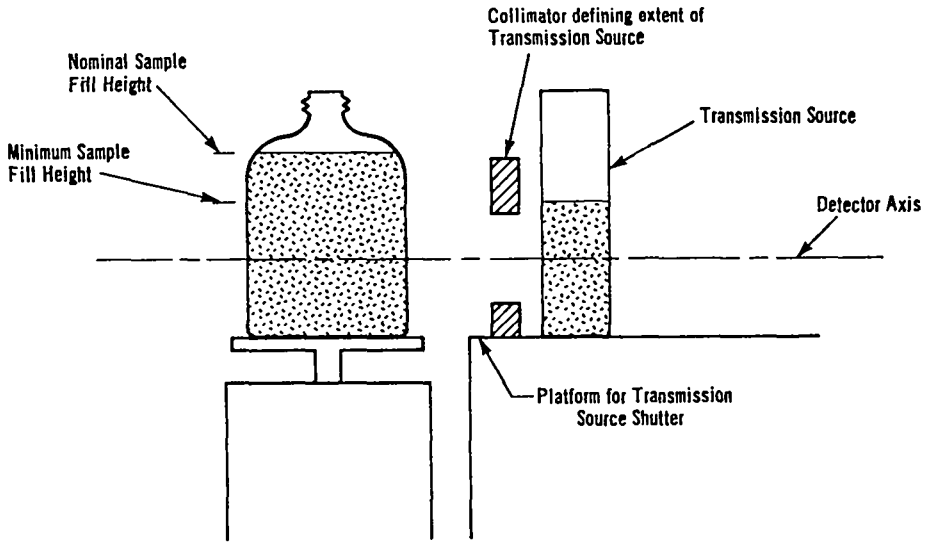

Fig. 12. Sample and transmission source positions for the low-resolution far-field assay configuration.

stable without assistance, and small drifts in the peak location can bias the peak area determination significantly. Low-resolution systems can use short amplifier time constants; consequently, they are less sensitive to pileup and deadtime effects. However, it is still good practice to limit the count rate to 10 000 counts/s or less. High-resolution systems should use a rate loss correction source,[4] enabling them to tolerate count rates up to 30 000 counts/s or more.

B. Data Analysis

The total count in the peak region, P, is subject to two background subtractions, B_1 and B_2, to obtain the net area, A.

$$A = P - B_1 - B_2 \quad . \tag{1a}$$

The statistical uncertainty in A is expressed by Eq. (1b).

$$\sigma(A) = \sqrt{P + B_1 + B_2} \quad . \tag{1b}$$

The first background, B_1, is the total count in the region just above the 185.7-keV peak region. The two regions, peak and background, should be the same width and are counted during the same data acquisition. When single channel analyzers are used, a reasonable window width for P is 160 to 210 keV; for B_1, a reasonable window width is 220 to 270 keV. If only one single channel analyzer is available, the two regions require two separate counts. This practice leads to difficulties if the background changes between the two counts. Background subtraction B_1 corrects for the Compton continuum under the 185.7-keV peak, which is due to higher energy gamma rays. Clearly, this subtraction is invalid if the background region contains a gamma-ray peak. The second background, B_2, is obtained from P - B_1 with no sample and no transmission source. If this background is nonnegligible, the assay position and shielding should be altered until it becomes negligible, if at all possible. Background subtraction B_2 corrects for 185.7-keV gamma rays that originate from somewhere other than the sample or transmission source. If B_2 is nonnegligible, the operator must determine that it does not vary, or else expect erroneous assays. High-resolution detectors generate spectra that allow for easier, more reliable peak area determinations.

The gamma rays emitted from within the sample may suffer attenuation before they reach the detector. The attenuation effects outside the sample container should be the same for all samples and reference materials; consequently, they can be ignored. The attenuation caused by the (empty) sample container is explicitly measured and accounted for in Eq. (2a).

$$CF(T_c) = \frac{1}{\sqrt{T_c}} \quad , \tag{2a}$$

where T_c = the container transmission at 185.7 keV and CF = the correction factor. The uncertainty in CF (T_c) is expressed in Eq. (2b).

$$\sigma[CF\ (T)_c] = 1/2\ \sigma(T_c) \quad . \tag{2b}$$

The container transmission is the net area determined with the empty container and transmission source in place, A(S + T), divided by the net area determined with only the transmission source and no container present, A(T), as expressed in Eq. (3a).

$$T_C = \frac{A(S + T)}{A(T)} \quad . \tag{3a}$$

The corresponding uncertainty is expressed in Eq. (3b).

$$\frac{\sigma(T_C)}{T_C} = \sqrt{\left(\frac{\sigma[A(S + T)]}{A(S + T)}\right)^2 + \left(\frac{\sigma[A(T)]}{A(T)}\right)^2} \quad . \tag{3b}$$

If different types of containers are used, the container transmission could be different. If the matrix is homogeneous and the ^{235}U is spread uniformly throughout the sample, the average self-attenuation can be related to the transmission through the sample. Consequently, a correction factor based on the sample transmission can be calculated. T_S = the sample transmission obtained from the measured transmission, T.

$$T_S = T/T_C \quad . \tag{4}$$

$$T = \frac{[A(S + T) - A(S)]}{A(T)} \tag{5a}$$

T_S and T are defined in Eqs. (4) and (5a), respectively, where A(S + T) = the net area determined with the sample and transmission source in place, and A(S) = the net area with the sample in place and the transmission source either removed or blocked with a shutter. The uncertainty in T is expressed in Eq. (5b).

$$\frac{\sigma(T)}{T} = \sqrt{\frac{\sigma^2[A(S+T)] + \sigma^2[A(S)]}{[A(S+T) - A(S)]^2} + \frac{\sigma^2[A(T)]}{A(T)}} \qquad (5b)$$

Small variations in homogeneity can be compensated for by using a line source instead of measuring the transmission at one point. Larger variations in homogeneity can be dealt with by using the SGS technique. Transmissions below 5% require a high-resolution system. At these low transmissions, the low-resolution technique requires very long count times and is susceptible to minor background fluctuations that may cause significant errors.

$CF(T_s)$ is obtained by an integration. Unfortunately, this integration does not have a closed form for most geometries of interest. It has been done numerically for 12 transmissions ranging from 0.004 to 0.400. These results were fitted to the quadratic in Eq. (6a).

$$CF(T_s) = a + b\,(\ln T_s) + c\,(\ln T_s)^2 \quad . \qquad (6a)$$

Table VIII lists the coefficients for three geometries. These coefficients result in CFs that agree with the integration values to ±0.4% or better for $0.004 < T_s < 0.400$. The uncertainty in CF resulting from an uncertainty in T_s is shown in Eq. (6b).

TABLE VIII

COEFFICIENTS FOR CORRECTION FACTORS

D/R	a	b	c
7:1	0.951830	-0.477093	0.0208312
10:1	0.950232	-0.484800	0.0224261
15:1	0.948981	-0.490709	0.0236976

$$\sigma[CF(T_s)] = \sqrt{[b^2 + c^2 (\ln T_s)^2]} \left(\frac{\sigma(T_s)}{T}\right) . \quad (6b)$$

If samples with different radii are assayed, different coefficients are appropriate for $CF(T_s)$.

The low-resolution detectors require the use of the same energy gamma ray for both the assay peak and the transmission measurement. The intensity of the 185.7-keV gamma ray from a uranium sample is limited by its self-attenuation; consequently, no strong sources are available. This limitation restricts transmission measurements to transmissions above 5%. High-resolution detectors can take advantage of stronger sources with gamma rays at nearby energies and reliably measure transmissions below 1%. If a transmission source other than ^{235}U is used in conjunction with a low-resolution system, its gamma-ray energy should be higher than and resolvable from 185.7 keV. This requires a correction to obtain T_s for the appropriate gamma-ray energy. Consequently, knowledge of the sample contents is required for correcting the measured transmission to the value for 185.7 keV. Equation (7) is used to compute the derived T_s.

$$T_s = (T_t)^{\alpha} , \quad (7)$$

where $\alpha = \mu_s/\mu_t$, s = the assay energy, t = the transmission energy, and μ = the mass absorption coefficient for the relevant material and gamma-ray energy.

The two CFs are used to generate the corrected counts, CC, from the net area, A.

$$CC = A \cdot CF(T_c) \cdot CF(T_s) . \quad (8a)$$

The associated uncertainty in CC is shown in Eq. (8b).

$$\frac{\sigma(CC)}{CC} = \sqrt{\left(\frac{\sigma(A)}{A}\right)^2 + \left(\frac{\sigma[CF(T_c)]}{CF(T_c)}\right)^2 + \left(\frac{\sigma[CF(T_s)]}{CF(T_s)}\right)^2} \quad . \tag{8b}$$

C. Calibration and Measurement Control

The general procedure for gamma-ray assay is outlined in the assay equation:

$$M = \frac{CC}{K} \quad , \tag{9a}$$

where M = the mass of ^{235}U and K = the calibration constant. The uncertainty is shown in Eq. (9b).

$$\left(\frac{\sigma(M)}{M}\right)^2 = \left(\frac{\sigma(CC)}{CC}\right)^2 + \left(\frac{\sigma(K)}{K}\right)^2 \quad . \tag{9b}$$

The calibration is determined with known reference materials and by inverting the assay equation, as shown in Eq. (10a).

$$K = \frac{CC}{M} \quad . \tag{10a}$$

The corresponding statistical uncertainty is shown in Eq. (10b).

$$\left(\frac{\sigma(K)}{K}\right)^2 = \left(\frac{\sigma(CC)}{CC}\right)^2 + \left(\frac{\sigma(M)}{M}\right)^2 \quad . \tag{10b}$$

The initial calibration should be based on repeated measurements of at least three reference materials. Because low-resolution systems typically have a

calibration that varies with the transmission, more than three reference materials may be needed to determine the calibration curve.

When the calibration has been established, it should be verified with the assay of a reference material each day that the system is used to measure unknowns. At least one verification assay should be done both before and after the assays of unknowns. If there is any reason to suspect a system malfunction, more frequent verification is appropriate. The low-resolution gamma-ray assay technique does not assay nonhomogeneous materials correctly, nor can it distinguish between homogeneous and nonhomogeneous samples. If previous results with certain samples indicate that a bias may exist in the calibration constant, but the verification assays indicate that the calibration is valid, then the uncertainty associated with the assay should be increased unless an investigation of inhomogeneities or sample fill heights invalidates the assay results. Without detailed knowledge of the present sample, any attempt to use previous results to correct the calibration is unjustified. Because this detailed knowledge is rarely, if ever, available, the user is left with the choice of either guessing the calibration parameters or increasing the uncertainty to reflect the lack of information.

The continued validity of the uranium content of the reference materials can be assured by a comparison with fresh solution standards. A somewhat less rigorous assurance is obtained by demonstrating one or more of the following:

- the response does not change with time;
- an SGS scan displays homogeneity with respect to transmission and corrected counts for each segment;
- a radiograph displays no signs of clumping;
- the response among the five standards is self-consistent;
- the response is consistent with the responses of other known uranium samples (for example, foils);
- physical security is employed to prevent tampering; or
- visual inspection indicates no deterioration of the reference materials.

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