LA-UR- 97-2741

Title: Performance of NDA Techniques on a
Vitrified Waste Form

CONF-970744--

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NOV 03 1997

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MASTER

Submitted to: Institute of Nuclear Materials Management 38th
Annual Meeting in Phoenix, Arizona on July 20 - 24,
1997

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Form No. 836 R5
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PERFORMANCE OF NDA TECHNIQUES ON A VITRIFIED WASTE FORM

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Abstract

Rocky Flats Environmental Technology Site (RFETS) is currently considering the use of vitrified transuranic (TRU)-waste forms for the final disposition of several waste materials. To date, however, little non-destructive assay (NDA) data have been acquired in the general NDA community to assist in this endeavor. This paper describes the efforts to determine constraints and operating parameters for using NDA instrumentation on vitrified waste. The present study was conducted on a sample composed of a plutonium-contaminated ash, similar to that found in the RFETS inventory, and a borosilicate-based glass. The vitrified waste item was fabricated at Los Alamos National Laboratory (LANL) using methods and equipment similar to those being proposed by RFETS to treat their ash material. The focus of this study centered on the segmented gamma scanner (SGS) with 1/2-inch collimation, a technique that is presently available at RFETS. The accuracy and precision of SGS technology was evaluated, with particular attention to bias issues involving matrix geometry, homogeneity, and attenuation. Tomographic gamma scanning was utilized in the determination of the waste form homogeneity. A thermal neutron technique was also investigated and comparisons made with the gamma results.

Introduction

Vitrification is currently being investigated at LANL and Pacific Northwest National Laboratory (PNNL) as the technology for the treatment of several waste materials at RFETS. One of the materials being considered for vitrification is low-fired ash. The project to develop a vitrification process for ash includes determination of an appropriate NDA technique for the analysis of the final vitrified waste form. The following study was conducted at LANL to determine the feasibility of utilizing various NDA instrumentation available at RFETS to measure these particular vitrified forms. The technique of most interest to RFETS and most focused upon in this study was the SGS with a 1/2-inch collimator, although the SGS with a 2-inch collimator was also included. The specific objective of this study was to determine if the SGS could meet an accuracy criterion within 10 % of the special nuclear material (SNM) content as measured by calorimetry and γ -ray isotopics. This study was performed on a full-scale vitrified ash sample prepared at LANL similarly to that anticipated at RFETS. The study focused on several factors known to decrease the accuracy of the SGS technique: sample density and homogeneity, end effects, and lump (self-attenuation) effects. A drum-sized TNC was also included in the investigation to provide an alternative in the event the SGS failed to meet the required level of accuracy.

Sample preparation

A full-scale sample was prepared using processing techniques as similar as possible to those anticipated at RFETS. The sample was prepared by heating a mixture of ash and borosilicate-based glass frit to 1000 °C to produce a fully-melted matrix that encapsulated the ash material. The frit was blended with sufficient ash to produce a Pu content of ~1 wt % in the mixture. The mixture was heated in a stainless-steel Vollrath #88080 can with a 1/32-inch thickness, 8-inch diameter, and 10-inch height. As an added precaution against a breaching of the container due to corrosion, this container was placed inside of a second container having a 1/16-inch thickness, 8 1/16-inch diameter, and 6 1/2-inch height. An ash item was chosen from the LANL inventory to simulate the ash at RFETS as closely as possible. The ash at RFETS was reported to have a Pu content of ~5 wt % and a high carbon, chloride, and fluoride content due to incomplete combustion of the original material's organic component. The most similar ash at LANL had a Pu content of ~9 wt % with

chloride and fluoride levels of 11.09 and 2.09 wt %, respectively. This LANL item had a loss-on-ignition value of 8.55 %, a density of 0.87 g/cm³, and a particle size of minus 40 mesh (452µm or 0.0165 inches).¹

Several observations were made after the preparation of the sample. The final height of the melted material in the sample was 2.6 inches. The inside of the container wall experienced spalling, with the residue ending up on the surface of the melt as black flakes. However, the spalling was not enough to jeopardize container integrity. In addition, the surface contained several bright yellow patches, thought to be due to incomplete dissolution of impurities in the ash and/or frit. The inside of the container and surface of the waste form are shown in Figure 1. The completed sample was prepared for the NDA study by bagging out the melt container and placing it in an overpack. The overpack was a ~1/16-inch thick steel container with a diameter of 9.9 inches and a height of 12.2 inches.

Baseline Determination

The first step in the measurement process was to establish the most accurate baseline SNM content possible for the vitrified ash sample. This was accomplished by measuring with calorimetry and γ -ray isotopics since that technique is known to introduce little or no bias.² The results are shown in Table 1.

Table 1
Calorimetry and Gamma Isotopics Data[†]

	Pu-238	Pu-239	Pu-240	Pu-241	Pu-242	Am-241 (µg/g Pu)
Mass %	0.01082	93.65381	6.14144	0.16893	0.02500	2048.8
Sigma	0.00132	0.21515	0.21560	0.00068	0.00125	32.2
Rel. Sigma	12.10 %	0.23 %	3.51 %	0.40 %	4.98 %	1.54 %
Total grams of plutonium on 26-Feb-97:					58.547	

[†]Specific power (watts/g-Pu) = (2.54667 +/- 0.01789) E-03 (0.70 %)

Sample power of 0.14910 watts measured on 26-Feb-97.

Since the calorimetric uncertainty² for this type of item is known to be ≤1 % and since the uncertainty on the specific power is reported to be 0.70 %, the uncertainty on the total value (58.547 g) should be on the order of 1 %. The primary drawback to using this technique on many items of this nature (i.e., low gram loading of Pu and relatively low heat conductivity of glass) is the long time to achieve calorimetric equilibration (about 8 to 12 hours).

SGS Measurement Issues

The next step was to measure the sample with an SGS, the preferred method at RFETS, in order to establish the feasibility of this technique³. Two such instruments reside in the NDA Laboratory at Los Alamos, one with 1/2-inch collimation used for can-sized items and the other with 2-inch collimation used mostly for drums, although smaller items can also be measured with reasonable accuracy. These instruments determine the quantity of SNM present in a sample by measuring the emitted γ radiation and comparing the corrected count rate with that from a known calibration standard. Since the γ rays are attenuated as a function of distance through the sample matrix, a correction factor must be applied. This factor is determined by using a γ -ray source of known strength (the transmission source) and measuring its absorption through the sample.⁴ The amount of absorption is a function of the sample density and uniformity. To help reduce the effects of matrix nonuniformity (or inhomogeneity), an averaging process is invoked by rotating and translating the sample during the measurement cycle. Data are therefore acquired for a number of horizontal slices spanning the sample height. These slices are summed at the end of the assay to obtain the total SNM content. If the

sample is too dense or nonuniform to allow proper functioning of the transmission source, either the measurement uncertainties will be intolerably large or there will be no reasonable assay result at all.

A special case of transmission difficulty, known as "end effects," occurs during the measurement at the top and bottom of every sample. Figure 2 shows a situation for a particular segment where counts are received into the detector with no transmission correction. As seen in the figure, end effects arise because the transmission measurement at the ends of the container does not representatively survey the material that is producing the γ radiation in that area (because the γ -ray acceptance cones do not totally overlap). These end effects are a special case of the more generalized uncertainties that arise when nonuniform (e.g., a bubble or any break, gap, or discontinuity in the matrix) items are measured.⁵ End effects can extend over a number of segments, depending on the instrument and sample geometry, and the result always biases the final answer low. The low bias occurs because the transmission source γ rays suffer less attenuation than those from the SNM in the matrix, resulting in correction factors for the affected segments that are too small. The degree to which the end-effects phenomenon affects the final answer is dependent upon the sample height to collimator (and segment step size) ratio, since a taller sample has a smaller fraction of affected segments.

Figure 1. NDA sample

Figure 2. End Effects

An additional difficulty arises if the SNM (plutonium in this case) is in the form of large particles or lumps of material. If the lumps are of sufficient radius, then the γ radiation will be attenuated enough while escaping the lumps to generate a bias. This phenomenon, known as self-absorption, is a completely independent process from the attenuation through the sample matrix discussed above. Self-absorption is a difficult SGS measurement issue. Although addressed in the past,⁶ the correction for self-absorption has yet to be adequately implemented and field tested.

It was known that sample (matrix) density and end effects were SGS issues that would affect the present study with the vitrified ash item. The other potential sources of bias were greatly reduced because every attempt was made during the sample preparation to ensure that the matrix was uniform and that the ash was evenly distributed throughout the matrix. Also, the -40 mesh size of the ash precluded that the Pu would be in lumps. To corroborate this belief, the sample was examined by real time radiography. No evidence (such as

dark or light areas or spots) of matrix nonuniformity or Pu clumping was seen. Further, the sample underwent a tomographic gamma scan in order to determine the homogeneity as a function of both radius and height. The resulting density and emission images didn't reveal anything that would be suspected of impairing the measurement. End effects, however, were unavoidable because of the small sample height (~2.6 inches) in relation to the 1/2-inch and 2-inch collimator sizes. It was also unclear if the transmission (and transmission uncertainty) would be sufficient through ~8 inches of borosilicate glass matrix having a density of approximately 2.6 g/cm^3 . Initial calculations revealed that the transmission would be <1 %. The validation would be to measure the item, check the transmission (and uncertainties) through the almost opaque region of the matrix, do the end-effects corrections, and compare the final mass results with the baseline result from calorimetry and γ isotopics. If the results are not biased low and the uncertainties are reasonable, then it can be assumed that there is little or no Pu lumpiness and/or matrix inhomogeneities and that the transmission is adequate.

SGS Measurement Results and Analysis

When the sample was received into the NDA Laboratory for the SGS measurements, the overpack (outer container) was opened to check if the inner container was centered and upright. As a result of the inner container having been "bagged out" (placed into two polyvinyl chloride bags) of the glove box line, it was tilted and leaning against the outer container wall. To correct this, paper was stuffed between the inner and outer containers to act as crude spacers to center and stabilize the inner container. Had that not been done, the actual item in the inner container would have been wobbling as the sample was rotated during the data acquisition, with the result that the transmission source would have seen varying diameters. That would have introduced the equivalent of another end-effects anomaly, this time from the side of the container.⁵ The final SNM result would then have been biased even lower.

As already indicated, the NDA Laboratory has two SGS instruments, one for can-sized items (1/2-inch collimation and segment size) and the other for drums (2-inch). Most of the SGS data in this study, shown in Tables 2 and 3, were acquired on the small-geometry instrument because 1/2-inch collimation is currently available at RFETS and the vitrified ash sample is a can-sized item. The data on the 2-inch SGS, shown in Table 3, were obtained in order to provide a means of cross-comparison with the 1/2-inch results. This proved to be very instructive and lent additional credence to the correctness of the analysis interpretation and results. For example, because of the larger collimation and segment step size of the 2-inch instrument, the final answer should be biased lower than that of the 1/2-inch if end effects are the primary bias generator. Comparing the results in the "Total SNM" columns in Tables 2 and 3, this is seen to be the case. Looking at the "Norm 1" column, which compares the total SNM results to the calorimetry and γ -isotopics baseline value, the 2-inch SGS is biased 64 % low compared with only 81 % for the 1/2-inch instrument. If the bias due to end effects is computationally corrected, and if the final corrected SNM results from both instruments compare favorably with the baseline value, that would be additional strong evidence that the end-effects corrections are being done properly and that end effects is the primary bias driver. Looking at the results in the "Corrected mass" and "Norm 2" columns of both tables, it is evident that end effects were able to account for all the bias.

Data were acquired at different initial vertical displacements to check for any bias dependence on starting position. The starting positions are shown in the "Offset" columns in Tables 2 and 3. The indication from the results is that any bias dependence on offset is less than the assay uncertainty and can be ignored. In addition, by obtaining 4 assays on the 2-inch SGS at successive initial offsets (1/2-inch vertical displacements), it was possible to obtain a set of combined data whose individual segment information matched very closely with that from the 1/2-inch instrument. To see this, it was necessary to cross-compare the individual segment information such as transmission and emission (uncorrected counts and/or rate).

Table 2
Assay Data for SGS with 1/2-inch Collimation

Run #	Total SNM (g)	Uncertainty (g)	% Uncertainty	Offset (in)	End effects (g)	% Correction	Corrected mass (g)	Norm 1 ^{†,⊕}	Norm 2 ^{‡,⊕}	Count time [§] (min)
1	49.801	4.764	9.57	0.00	10.5	21.1	60.3	0.85	1.03	20
2	52.378	6.148	11.74	0.25	8.8	16.8	61.2	0.89	1.05	20
3	48.179	5.692	11.81	0.12	8.9	18.5	57.1	0.82	0.98	20
4	47.065	3.072	6.53	0.38	9.8	20.8	56.9	0.80	0.97	20
5	44.278	1.524	3.44	0.25	11.0	24.9	55.3	0.76	0.94	20
6	43.390	1.800	4.15	0.25	11.0	25.4	54.4	0.74	0.93	20
7	47.441	5.521	11.64	0.00	10.0	21.0	57.4	0.81	0.98	20
8	44.675	1.855	4.15	0.00	9.1	20.3	53.8	0.76	0.92	28
9	49.596	6.000	12.10	0.12	10.5	21.2	60.1	0.85	1.03	28
10	47.362	1.537	3.24	0.00	9.5	20.1	56.9	0.81	0.97	60
Avg	47.417	3.791	7.84		9.9	21.0	57.3	0.81	0.98	
Std Dev	2.633	1.909	3.69		0.8	2.4	2.4	0.04	0.04	

[†] Norm 1 is the ratio of the measured total SNM to the characterized sample value of 58.547 g.

[‡] Norm 2 is the ratio of the end-effects-corrected mass to 58.547 g.

[⊕] These values can be read as % accuracy by subtracting 1.00 and multiplying by 100.

[§] The approximate time counting just the emitted radiation; i.e., not the empty space in the containers.

The end-effects bias was corrected manually since algorithms have not yet been built into the software. To perform the correction, it was first necessary to carefully examine the transmission and uncorrected assay count rates for each segment in the end-effects regions. It was easy from the transmission and emission segment data to identify many of the salient features of the sample such as the container lid, start of the different container thicknesses, start and extent of the actual item, and the bottom of the container. As mentioned already, it was very interesting and instructive to compare the segment data from the 2-inch and 1/2-inch instruments and match these features. The actual item starts and ends where the transmission has fallen to about 1/2 %. Since the item is 2.6 inches in height, there are roughly 5 to 6 segments of good assay data through this very dense region for the 1/2-inch instrument and only about 1 for the 2-inch. The end-effects regions comprise about 3 to 4 segments at the top and bottom of the actual item for both instruments. This region is identified at the top of the item as starting where the emission data just starts to exhibit counts above background and the transmission is almost 100 %, and ending in the item where the transmission is about 1/2 %. Therefore, in 3 to 4 segments the transmission has gradually fallen from almost 100% to 1/2 %. The region is identified at the bottom of the item in a similar manner.

Once the end-effects regions have been identified, the correction can be done. First, the partial corrections for each segment in the end-effects regions must be subtracted from the emission data segment by segment. The proper correction is then applied from an average of the correction factors for attenuation⁴ in the almost opaque region. These correction factors are easily obtained since they are printed with the segment data. The resulting additional corrected count rate is then added to the original and the ratio gives the percentage correction, which is shown as "% Correction" in tables 2 and 3. This % correction factor is used to correct the mass for that assay.

It should be noted that any bias built into the original mass calculation through the calibration will remain in the answer after the end effects bias is removed. For example, the 5 % high bias seen in the "Norm 2" column in Table 3 can be easily explained. Both the 2-inch and 1/2-inch SGSs were calibrated on a set of

2-liter plutonium can standards.⁷ The can standards are uniform mixtures of PuO₂ and diatomaceous earth in 3.75-inch diameter by 10.75-inch high stainless steel inner cans. Since these standards are filled to a height of only 7 inches, it is very likely that the 2-inch SGS would experience end effects on the order of 5 %. This 5 % bias is then built into the calibration and is propagated whenever that calibration is used. End effects for the 1/2-inch instrument are negligible on the 7-inch standards.

Table 3
Assay Data for SGS with 2-inch Collimation

Run #	Total SNM (g)	Uncertainty (g)	% Uncertainty	Offset (in)	End effects (g)	% Correction	Corrected mass (g)	Norm 1 ^{†,⊕}	Norm 2 ^{‡,⊕}	Count time [§] (min)
1	37.362	3.817	10.22	1.50	23.3	62.5	60.7	0.64	1.04	7
2	40.963	4.196	10.24	1.00	21.9	53.6	62.9	0.70	1.07	7
3	33.876	3.480	10.27	0.50	25.9	76.3	59.7	0.58	1.02	7
4	37.298	3.817	10.23	0.00	25.1	67.2	62.4	0.64	1.07	7
Avg	37.375	3.828	10.24		24.1	64.9	61.4	0.64	1.05	
Std Dev	2.506	0.253	0.02		1.5	8.2	1.3	0.04	0.02	

[†] Norm 1 is the ratio of the measured total SNM to the characterized sample value of 58.547 g.

[‡] Norm 2 is the ratio of the end-effects-corrected mass to 58.547 g.

[⊕] These values can be read as % accuracy by subtracting 1.00 and multiplying by 100.

[§] The approximate time counting just the emitted radiation; i.e., not the empty space in the containers.

TNC Measurement Results

Data were acquired on a drum-sized TNC to determine if that technique⁸ could be employed as a fallback in case the SGS, for whatever reason, was not viable. The data are presented in Table 4. It is apparent from the "Norm" column that there is a 16 % high bias with a rather large standard deviation (these results may be somewhat high because the TNC was found to be running about 6% high and was recalibrated on March 4). In addition, from TNC counting experience the data also exhibit a much higher than normal ratio of "Totals Rate" to "Reals Rate" (about a factor of 10 high). This information, coupled with the high levels of impurities in the sample (especially the large weight percentages of the chloride and fluoride components), points to (α , n) reactions as being the probable cause of the bias.

Table 4
Thermal Neutron Counter Data

Run #	Total SNM (g)	Uncertainty (g)	% Uncertainty	Norm [†]	Totals Rate (cts/s)	Reals Rate (cts/s)	Count time (min)	Date	Time
1	78.994	8.909	11.28	1.35	27701	87	30	3-Mar-97	13:58
2	77.994	8.880	11.39	1.33	27532	86	30	3-Mar-97	17:11
3	63.424	9.382	14.79	1.08	27888	68	30	5-Mar-97	17:17
4	57.463	9.605	16.71	0.98	26412	63	30	20-Mar-97	14:31
5	62.096	10.044	16.17	1.06	28113	68	30	20-Mar-97	16:19
Avg	67.994	9.364	14.07	1.16	27529	74			
Std Dev	8.804	0.439	2.32	0.15	591	10			

[†] Norm is the ratio of the measured total SNM to the characterized sample value of 58.547 g. These values can be read as % accuracy by subtracting 1.00 and multiplying by 100.

If the coincidence rate in the TNC is enhanced by induced fissions resulting from (α , n) reactions due to the high levels of impurities in the sample, then the enhanced coincidence rate can be corrected if the neutron multiplication is known. The multiplication can be estimated from Monte Carlo neutron transport calculations. From the preliminary data here, the bias appears to be about 15 % to 20 % from the induced multiplication. How well the correction can be done from Monte Carlo is difficult to estimate, but 3 % to 5 % is probably reasonable.⁹

Summary and Conclusions

The NDA study performed on this sample showed that SGS instruments with either 1/2- or 2-inch collimation can achieve an accuracy better than 6% relative to calorimetry and γ -ray isotopics. This accuracy is achievable, after correcting for the end-effects bias, for transmissions of about 1/2 % through the waste form and counting times of less than 30 minutes. These results are valid for ash material and graphite fines with the same degree of plutonium particle size, homogeneity, sample density, and sample geometry as the waste form used in this study. A drum-sized TNC was also included in the study to provide an alternative in the event the SGS failed to meet the 10% accuracy criterion. The preliminary indications are that this method will also achieve the required accuracy with counting times of ~30 minutes and corrections for an (α , n) bias due to the impurities in the sample. The bias corrections can be avoided in all cases if the instruments are calibrated on standards matching the items.

Acknowledgments

The authors wish to thank the following individuals for their assistance:

- Sandra Hildner, Darlene Gutierrez, and Eliseo Vigil for NDA laboratory support.
- John Rayburn for support on real-time radiography.
- Rudy Maez, Michael Padilla, and Jody Martinez for their assistance with the TGS measurements.
- Nancy Sheer and Lynn Foster for their assistance with the SGS instruments.

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