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DETECTION AND MEASUREMENT OF GAMMA-RAY SELF-ATTENUATION IN PLUTONIUM RESIDUES*

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ABSTRACT

A new method to correct for self-attenuation in gamma-ray assays of plutonium is presented. The underlying assumptions of the technique are based on a simple but accurate physical model of plutonium residues, particularly pyrochemical salts, in which it is assumed that the plutonium is divided into two portions, each of which can be treated separately from the standpoint of gamma-ray analysis: a portion that is in the form of plutonium metal shot; and a dilute portion that is mixed with the matrix. The performance of the technique is evaluated using assays of plutonium residues by tomographic gamma scanning at the Los Alamos Plutonium Facility. The ability of the method to detect saturation conditions is examined.

I. INTRODUCTION

Pyrochemical techniques have been used extensively in the DOE complex for plutonium recovery and purification. The residues from these processes are impure, containing high concentrations of Am-241, and inhomogeneous, consisting of a mixture of plutonium metal shot and plutonium dissolved in the salt. For example, in the molten salt extraction (MSE) process, americium is extracted from impure plutonium metal, producing a relatively pure metal product and an impure salt residue.

MSE residues are described by Christensen and Mullins[1] and by Longmire, et al.[2] A typical residue weighs about 2 kg, the bulk of which is a mixture of potassium and sodium chloride, and contains a small portion of the feed plutonium (on the order of 200 grams for a 4.5-kg run) in the form of $PuCl_3$ and plutonium metal shot. In addition, the salt contains 10—20 g of Am-241. Based on destructive analysis of these samples (by pulverizing the salt and passing the crushed material through a sieve), the metal shot has a distribution of sizes and may contain pieces as large as 10 mm in diameter (see Fig. 1). Other processes, such as electrorefining (ER) produce lower concentrations of Am-241 but contain significant quantities of metal shot.

There is a need for accurate, high-throughput assays of pyrochemical residues stored in can- and drum-sized samples. At Rocky Flats, there are roughly 5000 items containing molten salt extraction and electrorefining residues that will need to be assayed in future recovery and stabilization operations.[3] Pyrochemical salts are produced at the Los Alamos Plutonium Processing Facility and can also be found in transuranic waste at Los Alamos.

The difficulties posed by pyrochemical salts to nondestructive assay (NDA) are well-documented,[2,4] but are summarized here for completeness. Calorimetric assay (CAL/ISO) requires long equilibration times (6—8 hours). However, CAL/ISO is quite accurate. When the assumptions of the isotopic analysis are valid, the accuracy is approximately 2% for can-sized samples containing greater than 50 grams of plutonium. Passive neutron coincidence counting is routinely biased high due to the multiplication of neutrons produced by the (α,n) reaction following the decay of Am-241, and can be imprecise due to the high rate of uncorrelated events. Considerable effort has gone into the development of analytical methods and instrumentation to compensate for this effect, including the neutron self-interrogation technique and neutron multiplicity counting.[5,6] Finally, gamma-ray assay methods are almost always biased low due to self-attenuation of gamma rays emitted in the small pieces of plutonium metal shot.

Methods to correct for self-attenuation by plutonium metal shot, also known as lump-corrections, have been developed and applied to segmented gamma scanner (SGS) assays of pyrochemical salts.[4,7] The fundamental assumptions underlying the SGS lump correction methods are summarized as follows:

1. the SGS analysis is valid (e.g., the sample is uniform and homogeneous),
2. the instrument was calibrated with samples that contain no lumps,
3. the lumps are "microscopic" in the sense that they do not significantly influence the determination of the matrix attenuation coefficient,
4. the lumps are approximately spherical with a unique diameter, and
5. all of the plutonium is in the form of lumps.

When the assumptions are valid, the variation in the SGS assay with energy that is observed when lumps are present is given by

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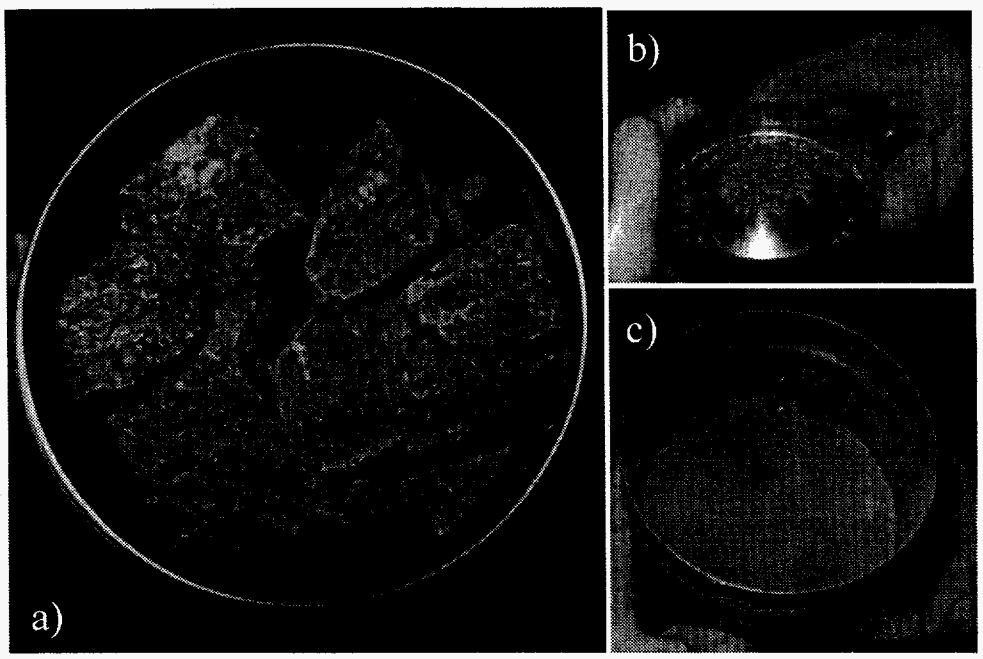

Fig. 1. Destructive analysis of an MSE salt carried out at the Los Alamos Plutonium Facility: (a) can containing chunks of salt; (b) large particles of plutonium metal separated from the matrix using a sieve; (c) particles that passed through the sieve, including the salt matrix contaminated with americium and plutonium chloride.

$$M(E) = MF_{\text{PuMetal}}(p, E), \qquad (1)$$

where $M(E)$ is the SGS assay at energy E, M is the mass of Pu-239, and F_{PuMetal} is the escape fraction for plutonium metal which depends on the diameter of the lumps, p, and the energy of the gamma ray. Plots of the escape fraction as a function of particle size are shown in Fig. 2 for the four gamma rays used in SGS lump-corrections.

A correction algorithm that uses ratios of SGS assays determined for selected gamma rays (e.g., 345 keV to 414 keV) to determine the size of the lumps was developed by Sprinkle and Hsue.[7] The mass is easily determined from Eq. (1) once the size of the lumps is known. It should be noted that assays at two energies are required to perform the correction. However, the procedure for determining lump size is usually repeated for several gamma-ray pairs to determine if the model and the observations are consistent.

Nearly all of the assumptions used to develop the SGS correction algorithm are invalid for pyrochemical salts. The salt matrix is nonuniform and inhomogeneous, the lumps have a distribution of sizes, and some portion of the plutonium is in the form of $PuCl_3$. Application of the lump-correction algorithm to SGS assays produces very little improvement over uncorrected results for pyrochemical salts.[4,7,8] Least-squares analysis of the SGS data, where the lump model was fitted to the energy-dependent SGS results, show that the lump model is not consistent with the data.[8] Reference 8 also reports on simulations that were used to assess the applicability of the single-lump-size model to samples that contained distributed lump sizes. The single-size model performed well, even in cases with a wide range of lump sizes; however, the study did not consider many cases in which a large portion of the plutonium had negligible particle size.

Additional effort was focused on determining the effect of bias caused by nonuniform matrix and source distributions on the quality of lump-corrections for 208-l drums.[9] For drum-sized samples, bias in SGS assays due to matrix and source position effects were shown to distort the energy variation at the lower gamma-ray energies, causing the lump-correction algorithm to fail. The same drums were assayed using an improved gamma-ray assay technique, tomographic gamma scanning (TGS).[10,11,12] Because the assumptions required for TGS analysis are far less restrictive than those for SGS (the distribution matrix and source material are determined by computerized tomography), the lump-correction was always successful when applied to TGS data.

However, measurements with a mobile TGS system, both at Rocky Flats and at the Los Alamos TRU site, were not

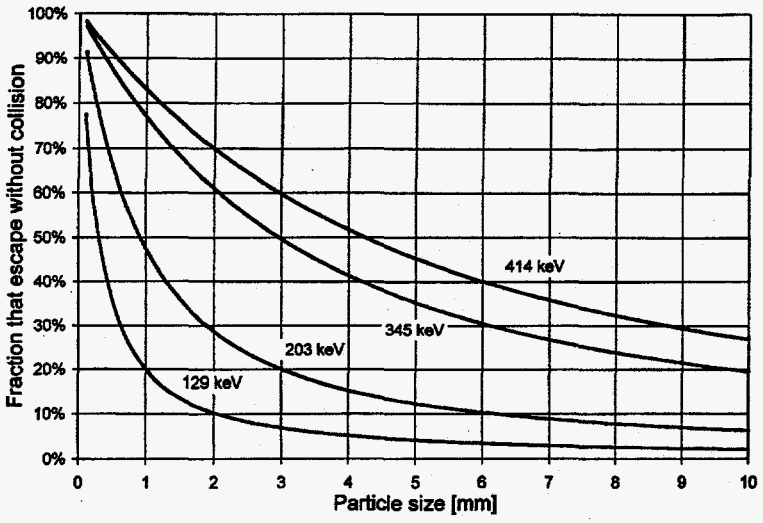

Fig. 2. Escape fractions for plutonium gamma rays as a function of particle size for spherical, metallic particles.

consistent with the controlled experiments in the laboratory. Lump-corrected TGS assays of residues and TRU waste containing salts with well-established reference values were biased low and the single-lump-size model was found to be grossly inconsistent with the energy-dependent TGS data. The results were very similar to those observed in lump-corrected SGS assays of pyrochemical salts. The correction factor for lumps based on the ratio of the 129-keV to 414-keV result was somewhat smaller than the correction factor obtained using the 345-keV to 414-keV ratio, and the correction factor showed a distinct increasing trend with energy.

In this paper, we propose a simple hypothesis for the observed variation of the correction factor that is consistent with the description of pyrochemical salts provided by Christensen and Mullins. The hypothesis leads to a slightly revised lump model and a correction algorithm that we can test for a wide range of plutonium residues, including pyrochemical salts. The data needed to test the new algorithm were obtained at the Los Alamos Plutonium Facility using a prototype TGS. In addition to proving our hypothesis, the results of the analysis can be used to provide a preliminary assessment of the performance of TGS for pyrochemical salts.

II. THEORY

Hypothesis: From the standpoint of gamma-ray NDA, the plutonium in pyrochemical salts, and other plutonium residues such as oxides, can be divided into a portion that consists of plutonium metal shot and a dilute portion that is mixed with the matrix material (i.e., as $PuCl_3$).

If the hypothesis is correct, the variation in the assay result with energy is given by

$$\mathbf{M}(\mathbf{E}) = \mathbf{M}\left[\alpha\,\mathbf{F}_{PuMetal}(\mathbf{p},\mathbf{E}) + 1 - \alpha\right], \qquad (2)$$

where p is the effective size of the metal shot and α is the fraction of the total mass of Pu-239 that is in the form of metal. The new model is similar to the old model in that it is assumed that the metal shot can be represented by a single lump size. From prior experience correcting simulated assays of samples with distributed particle sizes, this assumption is reasonably accurate.[8] The new model differs from the old model only in the treatment of particles of infinitesimal size. Attenuation by dilute plutonium mixed with the matrix is assumed to be fully accounted for by the gamma-ray transmission analysis and is expected to produce no observable energy variation. For TGS, where the assumptions of uniformity and homogeneity apply to relatively small volumes (on the order of 1 cm^3 for cans and 125 cm^3 for drums), this assumption is expected to be valid, especially when low density plutonium compounds are distributed over large regions.

Assay results at three energies are required to determine the parameters of the model. Lump size can be determined by examining the ratio of differences between assay results for different gamma-ray energies. For example, the following equation can be solved to determine lump-size:

$$\frac{\mathbf{M}(203)-\mathbf{M}(414)}{\mathbf{M}(345)-\mathbf{M}(414)} = \frac{\mathbf{F}_{PuMetal}(\mathbf{p},203)-\mathbf{F}_{PuMetal}(\mathbf{p},414)}{\mathbf{F}_{PuMetal}(\mathbf{p},345)-\mathbf{F}_{PuMetal}(\mathbf{p},414)}, \qquad (3)$$

where $\mathbf{M}(\bullet)$ denotes the mass determined by TGS at the selected energy. Once lump size is known, the M and α are easily determined. This direct approach, while conceptually simple, is not very useful in practice because p can vary considerably when different sets of gamma rays are used, even when the model is consistent with the data.

We prefer, instead, to fit Eq. (2) to the data using weighted least squares to determine the unknown parameters. The weights are determined by combining propagated statistical errors and estimates of the instrumental uncertainty of the assay for each energy. Constraints on each of the fitted parameters are imposed to avoid infeasible solutions. This approach uses all of the data to determine the parameters and is considerably more robust than the direct method.

III. EXPERIMENTAL

A prototype TGS developed by the Los Alamos Safeguards Program is currently at the Los Alamos Plutonium Facility and is undergoing testing and evaluation to assess the suitability of TGS for assaying residues and waste in can-sized containers and 208-l drums. The TGS technique uses transmission computerized tomography to form three-dimensional images of gamma-ray attenuating material. This information is used to correct emission tomographic data for nonuniform attenuation by the matrix, resulting in accurate, three-dimensional reconstructions of the distribution of nuclear material in the sample. Both the transmission and emission modes use high-resolution gamma-ray spectroscopy (HRGS). As in SGS, HRGS allows the intensity of selected gamma rays to be determined very accurately. Because both nonuniform attenuation by the matrix and the location of the emission sites are accounted for, TGS is very accurate for dense samples that are nonumiform and inhomogeneous. Detailed descriptions of TGS can be found in References 10, 11, and 12.

The prototype TGS was configured to assay can-sized samples (< 20 cm in diameter). Transmission and emission tomographic data sets were acquired using an adjustable collimator with high resolution (13 mm aperture) and low resolution (25 mm aperture) settings. The low-resolution scans, which correspond to images with 10x10x16 volume elements, are completed in less than an hour. The higher-resolution scans corresponding to 20x20x32 element images are completed in eight hours. The data will be used to assess the importance of spatial resolution for pyrochemical salt assays.

TGS images of a can-sized sample, roughly 20 cm in diameter and containing electrorefining salt, are shown in Fig. 3 along with radiographs of the salt. The transmission image was obtained using a collimator opening of 13 mm. Chunks of salt and the boundary of the inner container can be seen in the image. The emission image was obtained using a collimator opening of 25 mm. The highly localized distribution of plutonium in the sample is typical of the salts we examined.

To date, over 50 can-sized samples containing plutonium residues have been measured using the prototype TGS with both high and low resolution collimator settings. Residue categories include the following:

- MSE and ER salts;
- magnesium oxide crucibles;
- sand, slag, and crucibles;
- impure oxides and chlorides; and
- incinerator ash.

Most of the samples were assayed by calorimetry to obtain reference values needed to assess the accuracy of TGS. The samples were also assayed using SGS and passive neutron coincidence counting. In addition, a smaller number of the samples have been assayed using a neutron multiplicty counter optimized for pyrochemical salts. Only a portion of the TGS and neutron multiplicity data has been analyzed, and a full intercomparison will be available only after the completion of the measurement campaign. Preliminary results for TGS obtained by analyses of the data taken with the low resolution setting are available and were used to evaluate the new lump-correction model.

Calibration of TGS for the lump-correction study was accomplished using can-sized SGS standards described by Hsue, et al.[13] For self-attenuation analysis, care must be taken to select standards that have small particle size.

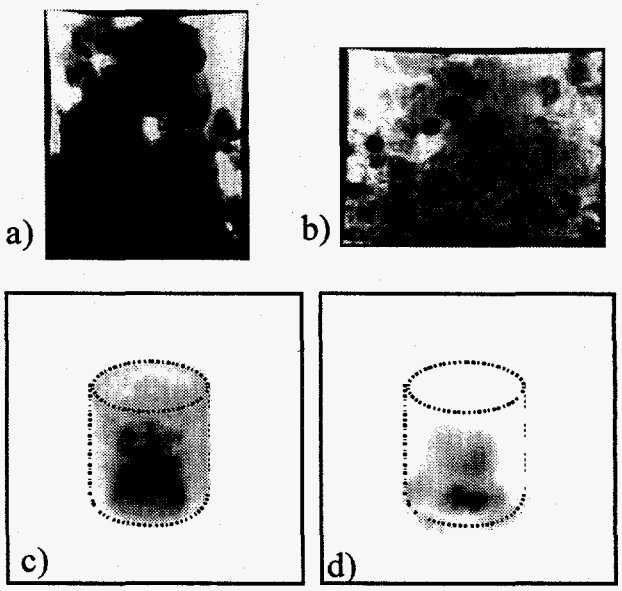

Fig. 3. Images of an electrorefining salt sample (XBLS5125); (a) x-ray radiograph of the inner can showing chunks of salt, (b) x-ray radiograph of a small portion of the sample, (c) radiograph of a TGS attenuation image with 13-mm voxel size, (d) emission image at 25-mm voxel size. The radiographs of TGS images were taken with a polar angle of 60 degrees.

Self-attenuation in particles with diameters as small as 100 microns is not negligible (see Fig. 1). The particle size in the SGS standards was determined using destructive analysis and is approximately 5 microns. With these standards, self-attenuation is negligible for all of the gamma rays of interest. More sophisticated calibration techniques that determine particle size along with the calibration constant for each energy are under development; these techniques will enable the restriction on particle size to be relaxed.

IV. RESULTS AND DISCUSSION

Twenty-six samples were analyzed using both the old and new lump-correction algorithms and the results of the corrections were compared with calorimetry. In the following discussion, we will refer to the old method in which all of the plutonium is assumed to be in the form of metal lumps as LCM. The new method, in which the plutonium is assumed to be a mixture of metal lumps and plutonium dissolved in the matrix, will be referred to LCMIX. Results of two representative samples are shown in Fig. 4.

In the first case (see Figure 4a), LCM was found to poorly fit the data. The lump diameter determined in the fit was 360 microns and the value of reduced chi-squared (χ^2_υ) for this fit was 3 with two degrees of freedom ($\upsilon = 2$). Based on the standard "goodness-of-fit" test, we conclude that it is unlikely that the assumptions underlying LCM are valid.[14] The LCM algorithm also failed to improve the TGS assay. The 414-keV result was biased low by 21% and the lump-corrected result provided by the LCS algorithm reduced the bias by a small amount (1%). In addition, the ratio method developed by Sprinkle and Hsue produced inconsistent correction factors. The correction factors obtained using ratios was 1.07 for the 129-keV to 414-keV ratio, 1.15 for the 203-keV to 414-keV ratio, and 1.34 for the 345-keV to 414-keV ratio.

In contrast, the LCMIX model produced an excellent fit ($\chi^2_\upsilon = 0.3$, $\upsilon = 1$). The fraction of mass in the form of plutonium metal was found to be 70% and the effective diameter of the metal particles was found to be 2.24 mm. The corrected mass of Pu-239 determined by LCMIX was 285 grams, which is within 2% of the reference value determined by calorimetric assay (281 grams).

In the second case (see Figure 4b), the quality of the fit produced by LCM was quite poor ($\chi^2_\upsilon = 10$, $\upsilon = 2$). LCM failed to improve the TGS assay and a similar trend was observed in the correction factor based on the ratio method. LCMIX produced an excellent fit to the data ($\chi^2_\upsilon = 0.5$, $\upsilon = 1$). The fraction of Pu-239 in the form of lumps was 60% and the effective lump diameter was 6.1 mm. Despite the excellent fit, LCMIX overestimated the total amount of Pu-239 by a substantial margin (24%).

Before accepting this result, we performed a test for saturation. Plutonium metal particles with diameters greater than about 1 cm can be considered infinitely thick, causing the assay at each energy to saturate (that is, the assay does not change appreciably with increasing particle diameter). Consequently, the sensitivity of the assay to particle size is very poor when the particles are large (see Fig. 1). To test for saturation, we simply assumed that the true lump size was large and fit the remaining parameters (α and M) to the data. We arbitrarily selected the diameter of the lumps to be 20 mm. The resulting fit is shown in Fig. 4b (circles) and is very similar to the original fit where p was treated as a free parameter. In fact, the reduced chi-squared value for the saturation test was 1.0 with two degrees of freedom, a highly reproducible fit. In general, saturation can be determined by comparing the χ^2_υ value obtained by LCMIX with the value obtained in the "saturation test" (p=20). If the difference is smaller than a threshold value (for example, $\Delta\chi^2_\upsilon < 1$), then saturation can be assumed.

LCMIX was applied to correct all 26 assays. Each case was screened for saturation using the "goodness-of-fit" test described above. Saturation was detected in six cases, each of which was rejected as a candidate for lump correction and marked as unsuitable for TGS analysis. Results for the remaining 20 samples are plotted in Fig. 5 for both LCM and LCMIX. There are a large number of cases for which LCM produced relatively small corrections. In each of these cases, quality of the fit produced by LCM was found to be quite poor. The total amount of Pu-239 (summed over all of the samples) predicted by LCM is lower than the calorimetric assay by about 10%. In comparison, the total amount of Pu-239 based on the 414-keV assay is lower than the calorimetric assay by about 20%.

The LCMIX algorithm made larger, and more accurate corrections than LCM and produced fits that were consistent with the data. The difference between the total amount of Pu-239 (summed over all samples) predicted by LCMIX and calorimetry was 49 ± 50 grams. The total amount of material in the 20 samples for which LCMIX provided a correction was 5489 grams. Consequently, the total amount of Pu-239 determined by LCMIX differs from the reference value by less than a percent. The average variation of individual results using the LCMIX algorithm was found to be $\pm$ 10%. A large portion of this variation is expected to be due to amplification of statistical variations in the counting data by the fitting algorithm. The error bars shown in the Fig. 5 are estimates of the statistical error based on the ratio

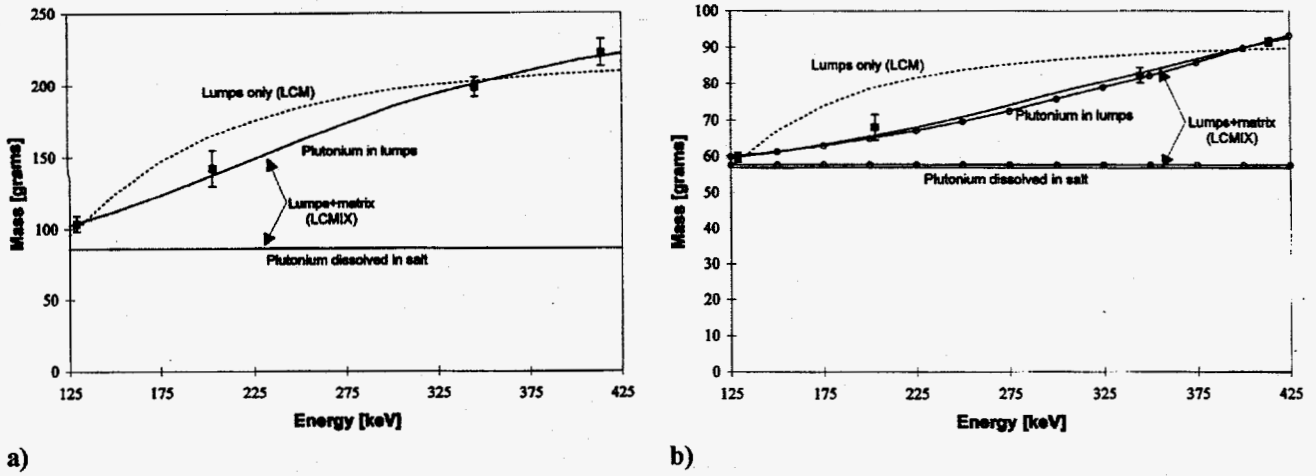

Fig. 4. Single-lump-size and mixture models fitted to multi-energy TGS assays for two samples. Two cases are represented: (a) the lump correction based on the mixture model (LCMIX) was successful; (b) saturation conditions were detected by LCMIX.

method and can be considered a lower bound for the variation in the corrected mass. Methods developed previously for estimating the variance of constrained estimators are being adapted to provide a complete sensitivity analysis for LCMIX.[15]

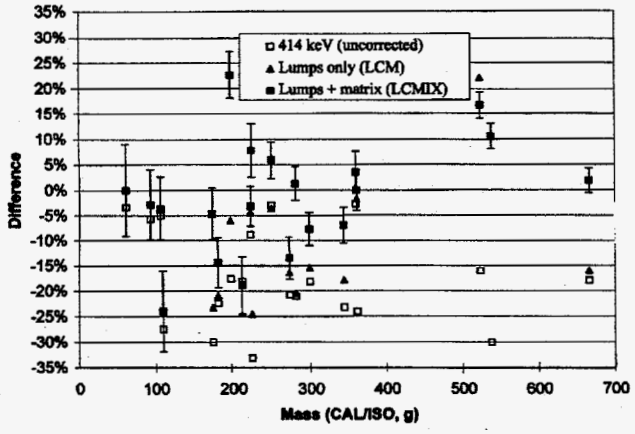

Fig. 5. Results of lump corrections applied to plutonium residues in small cans.

V. CONCLUSIONS AND FUTURE WORK

The primary conclusion that we draw from this work is that the mixture model (LCMIX) is superior to the models used in all previous efforts to correct for gamma-ray self-attenuation by lumps of plutonium. LCMIX conforms to an accurate physical model of pyrochemical salts and fits the gamma-ray assay data acquired for such samples, providing corrected results that are more consistent with calorimetric assay than the established method (LCM). The energy variation observed in correction factors (determined by the ratio method developed by Sprinkle and Hsue) further supports LCMIX, and is consistent with the assumption that there is some plutonium in the sample that causes little or no self-attenuation. LCMIX also identifies cases in which saturation conditions are present, which is essential for reliable lump corrections.

The primary limitation of LCMIX is that it requires assays for three or more Pu-239 gamma rays. Consequently, the technique may not work effectively for SGS, which can be biased considerably at low energy (for example, 129- and 203-keV). The technique is ultimately intended for use with TGS, which can provide accurate assays at all energies for a wide range of materials in can- and drum-sized samples. Results of the current evaluation will be used to optimize the configuration of the prototype TGS and to design new instruments that are capable of assaying plutonium residues with improved accuracy.

Another useful application of the LCMIX model is determination of the metal content of residues for recovery and stabilization. Depending on the process used, it is likely that the ability to recover plutonium from salts is strongly correlated with the amount of metal already present in the material. Samples with small quantities of metal may not be worth recovering. The LCMIX model, combined with a reference technique such as calorimetry, could be used as a nondestructive sieve, providing estimates of the size of the metal particles and the portion of the plutonium that is in the form of metal. Calorimetric assay would provide an accurate estimate of the mass, leaving only two parameters (α and p) to be determined by LCMIX from TGS data. The results of applying this techniques to the samples assayed at the Los Alamos Plutonium Facility are shown in Fig. 6.

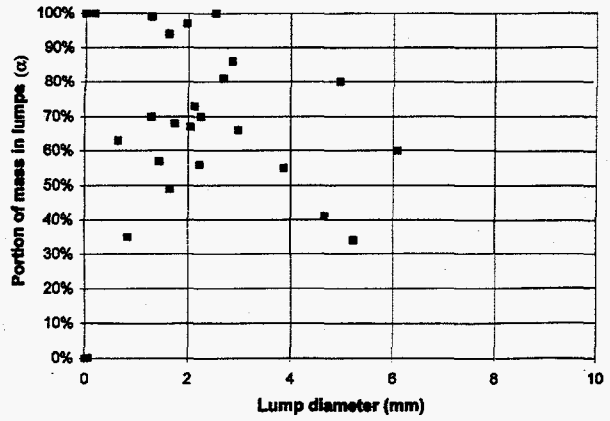

Fig. 6. Sieving plutonium metal with CAL/ISO and TGS.

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