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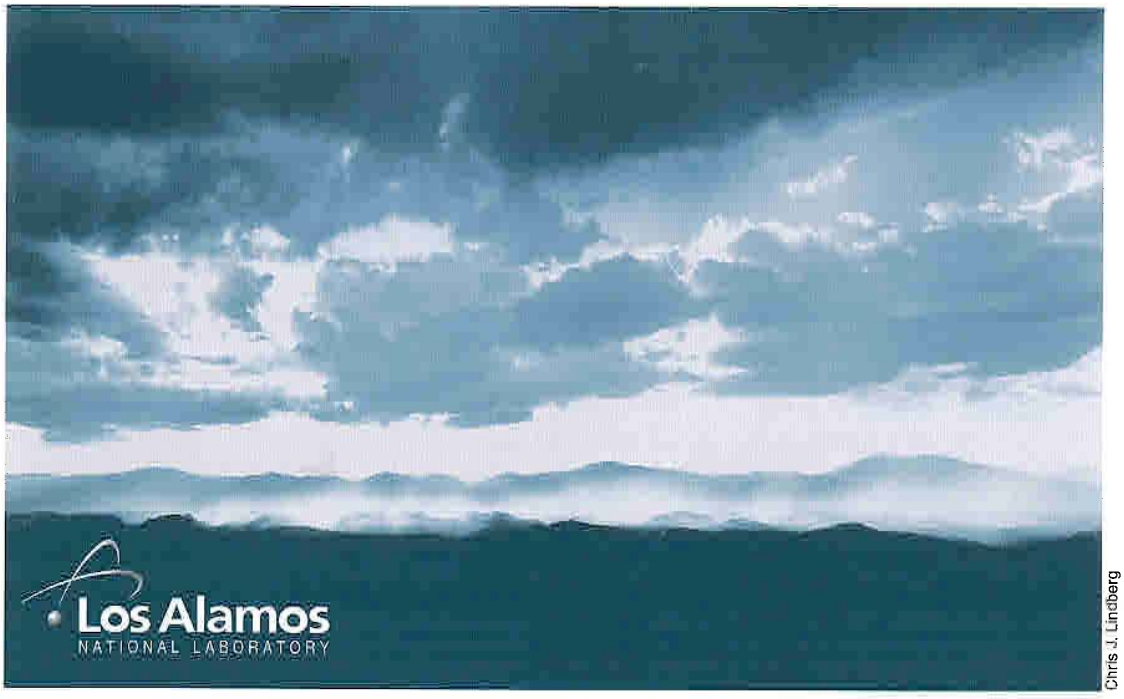

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ABSTRACT

The Safeguards Science and Technology Group at the Los Alamos National Laboratory has accumulated a large quantity of high-purity germanium (HPGe) detector gamma-ray spectra in support of the development of the FRAM (Fixed Energy, Response Function Analysis with Multiple Efficiencies) gamma-ray isotopic analysis software.

These data, acquired over a period of 15 years, represent a variety of planar and coaxial HPGe detectors, analog and digital data acquisition electronics, and represent both laboratory and facility measurements. All data are multiple measurements from samples with well-documented isotopic composition from mass spectrometry measurements.

We will report the results of rigorous statistical analyses of FRAM analysis results. The presentation will discuss the errors in FRAM analyses arising from the choice of detector type and analysis energy region and document the errors arising from sample-dependent and analysis-dependent effects.

INTRODUCTION

The FRAM gamma-ray isotopic analysis software was first fielded at the Los Alamos Plutonium Facility in 1988.[1] References 2 and 3 provides information on the technique itself, subsequent versions of FRAM, measurement applications, and an extensive list of references.

Gamma-ray isotopic analysis is one of a very limited number of nondestructive assay (NDA) techniques that do not require calibration with representative standards. The technique is applicable to measurement of the isotopic composition of plutonium in the widest possible variety of materials because the measurement method does not depend upon the physical or chemical form of the sample, the sample's matrix material, the measurement geometry, or the type or composition of the sample container. The FRAM isotopic analysis software can analyze spectra from most any measurement situation that allows detection of plutonium gamma rays from all (except ^{242}Pu) the plutonium isotopes.

While the measurement technique does not require calibration with standards of known isotopic composition, the method is confirmed and validated with measurements of samples with documented isotopic distributions and the comparison of the measured and documented accepted values is used to make small adjustments in the gamma-ray branching fractions used by FRAM.

Los Alamos has a large number of plutonium-bearing samples with documented isotopic distributions. We have archival gamma-ray spectral data from many of these samples going back to 1988 when FRAM was first put into use. For some of the documented samples, we have multiple archival data sets separated in time by nearly a decade. We have published[2, 3] simple analyses of the biases in the measurement of these standards. In this report we analyze these archival data with

more sophisticated Analysis of Variance[4] (ANOVA) methods. With these methods we show that the errors between the measured and accepted values are dependent upon the energy region of the analysis and in some cases are dependent upon the specific sample itself. The analysis method also enables us to identify "outliers" that we believe are most likely due to relatively large errors in the documented accepted values for the isotopic distributions.

SOURCES OF ERROR IN GAMMA-RAY ISOTOPIC ANALYSIS

A detailed discussion of the errors affecting gamma-ray isotopic analysis measurements is beyond the scope of this document but may be found in Ref. 2. Some of the error sources are listed below with a discussion of their effect on the results of the ANOVA analysis.

Counting Statistics

A random error arising from the statistical uncertainties in the net peak areas used in the analysis is present in every measurement. The random error is dependent upon the measured isotope, its isotopic fraction, the counting time, counting rate, and many other measurement-related effects. The analysis in this paper captures the random error from the repeated measurements analyzed for each sample.

The FRAM software also predicts the random error from counting statistics for each measurement. This prediction, as documented in Ref. 2, is in reasonable agreement with the random error observed from repeated measurements. The agreement documented in Ref. 2 means that the predicted random error from the FRAM software can be used in propagation of variance calculations.

Sample Composition Characteristics

The elemental makeup of the sample influences self-absorption in the sample and thereby influences the shape of the relative efficiency curve. Version 4 of FRAM accounts for this effect by allowing up to three different elements or compounds to define the matrix. The result is almost always a good fit to the relative efficiency points, within its range of definition. The accuracy of the relative efficiency curve is reduced somewhat if it is extrapolated outside its range of definition. Relative efficiency curve effects can result in a sample-dependent bias.

Branching Ratios

The accuracy of the branching ratios (gamma rays per decay) of the gamma rays used in the analysis directly affects the accuracy of the analysis. The branching ratios are fundamental nuclear constants, albeit somewhat imperfectly known, that are part of the parameter file governing the analysis. We carefully examine the analysis results before we use a newly developed parameter file. If we still observe biases, even after careful setup of the parameter file, we will generally make an adjustment in the branching ratios to reduce or eliminate the bias. The adjustments are usually small and within the uncertainties of and differences in published values for the branching ratios.

The adjustments result in overall biases for a given parameter file that are quite small and apply to all samples analyzed with the parameter file.

Peak Area Determination

Background Shape. The shape of the background continuum in the gamma-ray pulse height spectrum is dependent upon many parameters and characteristics of the sample and the sample-detector measurement geometry. Correctly defining the shape of the background continuum underneath a peak region is one of the most important factors influencing the accuracy of the peak area determination. An inaccurate definition of the background continuum is one of the largest sources of bias in the peak area determination and can lead to sample dependent biases.

Interferences. An unexpected peak (a peak not accounted for in the peak list in the parameter file) appearing in an analyzed region of the spectrum, may bias the analysis of the designated peaks in the region. Unaccounted-for peaks can be a problem in the analysis of the arbitrary sample, but are not a factor in the analysis of these archival spectra because the archival spectra contain only peaks that are accounted for in the analysis.

^{242}Pu Correlation

FRAM, like all isotopic analysis codes, uses a correlation to predict the ^{242}Pu isotopic fraction. Because of the normalization condition, an error in the prediction of the ^{242}Pu isotopic fraction will propagate into errors in all of the other isotopic fractions, even if all of the isotopic ratios were measured correctly. This source of bias is not present in these analyses because the known ^{242}Pu isotopic fraction was operator-entered for every analysis.

SAMPLES USED FOR ARCHIVAL SPECTRAL DATA

Los Alamos possesses archived gamma-ray spectra dating from 1988. All spectra come from samples with documented isotopic distributions. Some of the samples are Certified Reference Materials.Others may be categorized as Working Reference Materials, and still other samples have characterizations from multiple laboratories or multiple measurements at the same laboratory. Other samples are characterized with a single, traceable mass spectrometry measurement.

The gamma-ray spectra from these samples have been acquired with a wide variety of detectors and data acquisition electronics representing the state-of-the-practice at the time of the data acquisition. From 1988 through the mid 1990s the spectra were acquired using high-quality analog spectroscopy components. The most recent data were collected by using digital spectroscopy systems. Most of the data come from equipment that was set up and adjusted by experienced gamma-ray spectroscopists; almost without exception, the data come from high-quality HPGe detectors free from visible radiation damage and peak tailing.

The data used in these analyses capture variability resulting from different detector characteristics within a detector type and from different electronic characteristics representing the state-of-the-practice over a period of nearly 15 years. The data also represent a mix of laboratory measurements and facility measurements using standard facility equipment. In this manner we feel that the analysis will represent the capabilities of the FRAM software under good measurement conditions. A description of the plutonium samples and their characterization is given in Ref. 3.

THE DATA GROUPS

The FRAM isotopic analysis software is very versatile, being able to analyze data in different energy ranges from both planar and coaxial detectors. Historically, FRAM was used with planar

HPGe detectors to analyze data in the energy range from 120 keV to 420 keV. Subsequent advances allowed FRAM to be used to analyze spectral data from coaxial HPGe detectors. The greater efficiency of coaxial detectors allowed analysis of weaker high-energy peaks that were too weak for analysis in planar detector spectra. The higher-energy gamma rays are more penetrating and escape in measurable fractions from shielded samples or samples in heavy-walled containers. Consequently, FRAM routinely analyzes coaxial HPGe detector data in the energy range from 120–450 keV when the sample container is "thin" and analyzes data in the 200–800 keV range when the sample is shielded or contained in a heavy-walled container.

The above cases form the basis for dividing the archival data into three groups for analysis. The characteristics of the three data groupings are described in Table 1.

Table 1. Characteristics of the Data Groups

	Group 1 (G1)	**Group 2 (G2)**	**Group 3 (G3)**
Energy Range (keV)	120–420	120–450	200–800
Detector Type	Planar	Coaxial	Coaxial
No. of Samples	33	46	53
No. of Measurements	494	749	826
Avg. Meas./Sample	15.0	16.3	15.6
Parameter File	Planar_Widerange3	Coax_Widerange3	ShCoax_Widerange3

Groups 2 and 3 arise from the same group of spectra with analysis taking place in different energy ranges. Seven of the samples in this group are shielded with lead and cannot be analyzed in the 120–450 keV range, accounting for the difference in sample size between Group 2 and Group 3.

FRAM Parameter Files

A FRAM analysis is guided by an extensive set of parameters contained in a parameter file. These parameters specify the isotopes to be analyzed, the peaks to be used in the analysis and direct the details of how each peak contributes to the analysis. The parameter file also contains fundamental nuclear physics parameters for the half-lives and gamma-ray branching fractions. All of the data in each individual group were analyzed using the same parameter file. The three parameter files in Table 1 are the standard parameter files customarily used for these analysis conditions and are part of the standard FRAM distribution.

ERROR ANALYSIS

We analyze data from each of three measurement groups. The characteristics of the groups are defined on the basis of physical features as described in Table 1.

Error Model

Assume that the measurement error within a given group can be modeled as

$$X_{ij} = T_i + T_i^{\alpha_B} B + T_i^{\alpha_S} S_i + T_i^{\alpha_R} R_{ij}\,, \qquad (1)$$

where i indexes items within the measurement group, j indexes repeated measurements on the item, X_{ij} is the measured parameter, T_i is the true value of the measured parameter, B is the group-specific bias, S_i is the item-specific systematic error, and R_{ij} is the random error. The coefficients α_B, α_S, and α_R determine how the B, S, and R errors vary as T_i changes. For example, if $\alpha_R = 0$ (1) then the random error model is additive (multiplicative), and if $0 < \alpha_R < 1$ then the random error model is between additive and multiplicative. The item averages, between-item variance, and scaled within-item variance case are used to estimate model parameters.

Other error models are possible, but (1) is common. All errors are random at some stage, which we denote, for example, as $R_{ij} \sim N(0, \sigma_R)$ (normally distributed with mean zero and standard deviation σ_{Ri}) and $S_i \sim N(0, \sigma_S)$. The term B would change in future calibrations, and is, therefore, random across calibrations, so $B \sim N(0, \sigma_B)$.**

We assume that a "gold-standard" method (mass spectrometry) provides the true value T with negligible (and, therefore, assumed to be 0) measurement error (see Topic 4).

We chose values for the coefficients α_B, α_S, and α_R by experimenting with trial values for each coefficient to find values that led to best out-of-sample prediction in a cross-validation (CV) exercise. In the CV we randomly selected approximately 2/3 of the samples to train (choose coefficients) and the other 1/3 to test. The performance measure was the ratio of the predicted standard deviation of the sum of test measurements to the observed sum of measurements. Ratios near one indicate good agreement and therefore good coefficients. We also tested this for the sample sizes available using simulated data and confirmed that this CV procedure could reliably choose an additive (multiplicative) model when the simulated data followed an additive (multiplicative) model.

We considered each of the six assays: ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{241}Am, and Specific Power (P_{eff}). We ignored ^{242}Pu because the user sets this value and also ignored ^{240} Pu_{eff} because it is a linear combination of the even plutonium isotopic fractions, closely tracking ^{240}Pu.

**Gamma-ray isotopic analysis measurements are not calibrated in the usual sense of the term. The group-specific bias arises from the effect of literally hundreds of parameters that define an analysis parameter file, as well as from the effect of the assumptions used in the analysis and the imperfect nature of the analysis itself. A different set of parameters defining a new parameter file will likely produce a different group-specific bias, changing B. While we do not consider this to be a calibration, a new parameter file has a similar effect statistically as does a new calibration (used in the usual sense).

Analysis Results
Consider the following for the groups defined in Table 1.

Topic 1. Do the error magnitudes depend on the true values, or on other measurements that would provide good estimates of the error variance?

Results: A multiplicative model fits well for each group and for each error type, although outliers can impact the chosen value of $\alpha_S = 1$ in particular.

Topic 2. Estimate σ_B, σ_S, and σ_R using all samples or using all samples except outlying samples.

Results: Generally, removing outliers reduced the estimate of σ_S but not dramatically, so for brevity, in Table 2 we present estimates only for the case in which all samples (including outliers) were used.

Table 2. ANOVA Analysis of Three, Detector-Type/Energy-Analysis-Range Data Sets

Assay	Estimate of σ_R (% RSD)			Estimate of σ_S (% RSD)			Estimate of ratio σ_S / σ_R			Std. Dev. of Relative Biases (% RSD)			Estimate of σ_B (% RSD)		
	G1	G2	G3	G1	G2	G3	G1	G2	G3	G1	G2	G3	G1	G2	G3
^{238}Pu	3.2	7.3	8.2	1.6	2.3	7.6	0.5	0.3	0.9	1.0	3.5	7.4	0.09	0.8	0.9
^{239}Pu	0.2	0.2	0.4	0.1	0.1	0.4	0.6	0.4	0.9	0.1	0.1	0.4	0.02	0.02	0.06
^{240}Pu	1.4	1.9	2.5	0.7	0.8	1.6	0.5	0.4	0.7	0.8	1.0	1.6	0.06	0.006	0.04
^{241}Pu	0.4	0.5	0.8	0.6	0.6	0.7	1.6	1.1	0.9	0.5	0.5	0.8	0.2	0.03	0.4
^{241}Am	1.6	0.8	0.6	1.3	0.9	0.8	0.8	1.1	1.2	1.2	0.9	0.8	0.3	0.5	0.3
P_{eff}	0.3	0.3	0.5	0.2	0.2	0.5	0.8	0.6	0.9	0.1	0.2	0.5	0.05	0.1	0.1

Columns 2, 3 and 6 give estimates (as percent relative standard deviation) of σ_R, σ_S, and σ_B, respectively, for each of the 3 groups (see Table 1) denoted G1, G2, and G3. Column 4 estimates the ratio σ_R/σ_S, which estimates the relative magnitudes of pure random error and item-specific systematic errors. Column 5 is the percent standard deviation of relative biases, which is a rough estimate of σ_S that does not account for the impact of random error R in the relative biases (this rough estimate will usually slightly overestimate σ_S, depending on absolute and relative sample sizes for each item).

The estimate of σ_R represents a global characterization of the random measurement error (basically counting statistics) for FRAM drawn from the specific data sets used in the analysis. A FRAM user may obtain different random error components when using different counting times or counting rates from those represented in the data sets. However, because the FRAM data sets come from measurements made using realistic counting times and counting rates, these estimates are valid for many measurements made under field conditions.

Topic 3. Outlier Detection.

Result: Informal graphical methods, as well as more formal quantitative threshold tests, suggest that some items are outliers either because the accepted value is highly suspect (large estimate of S_i in Eq. 1) or because the precision is unusually bad (large estimate of σ_R). We did not remove the samples with known characterization errors from the data sets, preferring to leave them in as a check to see if the analysis would flag them as outliers. The analysis correctly flagged samples with known characterization problems. The outliers did not drastically change the value of σ_S, and the values in column 3 of Table 2 can be considered to be conservative. (That is, they slightly overstate the value of σ_S, but not dramatically.)

Topic 4. Uncertainty in Standards.

Result: We have ignored uncertainty in the mass-spectrometry-based accepted values because we do not have an accepted value for the mass spectrometry uncertainty for each item. Therefore, column 3 in Table 2 estimates the combined effect of item-specific systematic errors from both FRAM and mass spectrometry. This implies that item-specific errors from FRAM are acceptably small (the estimates of σ_S/σ_R in column 4 are mostly less than 1). Because mass spectrometry errors are expected to be very small for these items, it is unlikely that subtracting the impact of mass spectrometry errors would render the FRAM-based item-specific errors negligible. We therefore consider the estimates of σ_S to be upper bounds, but still reasonably close to the true values. Another way of looking at this is that σ_S represents the item-specific systematic error that could be quoted a priori for a FRAM isotopic analysis measurement on good materials. The values for σ_B validate the generally quoted claim that the isotopic fractions for an arbitrary sample can be measured with a group-wide bias of less than 1% relative.

Topic 5. Bias Adjustments, "Random" and "Systematic" Errors, and Associated Error Propagation. For the estimates for σ_B in Table 2, the data suggest that because of item-specific biases, a bias-adjusted result actually has larger bias than the non-bias-adjustments results in Table 2. Bias adjustment possibly does more harm than good here!

The estimates of σ_S and σ_R could be added in quadrature into an effective random error variance for variance propagation across assays of multiple items (because S_i is random across items). However, it would still be necessary to separately estimate σ_S and σ_R as we have done here because σ_S and σ_R each have a different impact on σ_B and because σ_S would be ignored if we relied completely on precision estimates to estimate the effective random error standard deviation.

The values for σ_B in Table 2 represent the average uncertainty to be expected for a large number of samples measured with the given detector type and analyzed in the stated energy range with the specified parameter file. These non-bias-adjusted results are slight overestimates of σ_B that result from using the absolute value of the mean bias. The values for σ_B are mostly smaller than the sample-specific systematic error σ_S.

CONCLUSIONS

We have completed an ANOVA analysis of three large gamma-ray spectroscopy data sets. The data sets consist of gamma-ray spectra from plutonium samples analyzed with the FRAM isotopic analysis software. We documented the effect of commonly used detector type (planar or coaxial)

and analysis energy range (120–420 keV, 120–450 keV, 200–800 keV) combinations on the random error, item or sample-dependent systematic error, and group-specific (detector-type/energy-analysis-range combination) bias. The ANOVA analysis used the results of over 2000 analyses on 132 items.

The random errors (counting statistics) found in this analysis agree with what is customarily seen in facility measurements at Los Alamos. The item-dependent systematic errors are generally <1% (relative) for all isotopes except ^{238}Pu as expected. This is interpreted as the systematic error to be expected a priori. The group (detector-type/energy-analysis-range) bias was found to be smaller than the item-dependent systematic error.

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